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Impact stratigraphy: Old principle, new reality

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ABSTRACT

Impact stratigraphy is an extremely useful correlation tool that makes use of unique events in Earth's history and places them within spatial and temporal contexts. The K-T boundary is a particularly apt example to test the limits of this method to resolve ongoing controversies over the age of the Chicxulub impact and whether this impact is indeed responsible for the K-T boundary mass extinction. Two impact markers, the Ir anomaly and the Chicxulub impact spherule deposits, are ideal because of their widespread presence. Evaluation of their stratigraphic occurrences reveals the potential and the complexities inherent in using these impact signals. For example, in the most expanded sedimentary sequences: (1) The K-T Ir anomaly never contains Chicxulub impact spherules, whereas the Chicxulub impact spherule layer never contains an Ir anomaly. (2) The separation of up to 9 m between the Ir anomaly and spherule layer cannot be explained by differential settling, tsunamis, or slumps. (3) The presence of multiple spherule layers with the same glass geochemistry as melt rock in the impact breccia of the Chicxulub crater indicates erosion and redeposition of the original spherule ejecta layer. (4) The stratigraphically oldest spherule layer is in undisturbed upper Maastrichtian sediments (zone CF1) in NE Mexico and Texas. (5) From central Mexico to Guatemala, Belize, Haiti, and Cuba, a major K-T hiatus is present and spherule deposits are reworked and redeposited in early Danian (zone P1a) sediments. (6) A second Ir anomaly of cosmic origin is present in the early Danian. This shows that although impact markers represent an instant in time, they are subject to the same geological forces as any other marker horizons—erosion, reworking, and redeposition—and must be used with caution and applied on a regional scale to avoid artifacts of redeposition. For the K-T transition, impact stratigraphy unequivocally indicates that the Chicxulub impact predates the K-T boundary, that the Ir anomaly at the K-T boundary is not related to the Chicxulub impact, and that environmental upheaval continued during the early Danian with possibly another smaller impact and volcanism.

Keywords: stratigraphy, impacts, Chicxulub, K-T boundary.

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INTRODUCTION

The law of superposition—simply stated, that *in any undisturbed sediment sequence the oldest bed is at the base and the youngest at the top*—has served generations of geologists and led the advance in understanding Earth's history. It has remained the fundamental principle of *Stratigraphy* in relative age dating, permitting the reading of any rock record as an ordered sequence of events from oldest to youngest, regardless of the time period in which it was deposited, or the nature of events that caused their deposition. *Biostratigraphy* is arguably the most reliable and commonly applied age dating technique in stratigraphy. It makes use of the fossil record and its unique evolutionary events, such as species originations and extinctions, unique population turnovers, and individual species blooms, and ties these to the paleomagnetic and radiometric records.

As radiometric dating has steadily improved to error bars of only a few hundred thousand years and scientists have tried to decipher and date the sequence of critical events in Earth's history with ever greater age control, the law of superposition has remained more relevant than ever. This is particularly so for major mass extinctions where a sequence of closely spaced events over a few hundred thousand years may have contributed to the catastrophic demise of life evident in the fossil record. But frequently, radiometric dating cannot decipher the order of such closely spaced events because they may fall within the error limits of the dating methods. In such cases, the only way to determine the time sequence of events leading up to the catastrophe—and hence the potential cause and effect—is the stratigraphic relationship of these events to each other as seen in the sediments and fossils within each rock unit that reveal environmental and biotic effects over time. Stratigraphy and biostratigraphy are thus the handmaidens of geologic history.

During the last decade, the old law of superposition, and stratigraphy and biostratigraphy in particular, has come under attack by what could be called *impact exuberance*. This new reality is driven largely by the belief that large impacts must cause catastrophic mass extinctions and that the telltale evidence of impacts, such as impact breccia, glass spherules, shocked minerals, and iridium anomaly, must therefore be coincident in time with the biotic catastrophe regardless of the sediment layers separating the impact signals from the mass extinction. The most egregious example of this impact exuberance is the K-T boundary mass extinction and the Chicxulub impact. The theory that a large impact caused the mass extinction is widely considered as substantiated by the iridium anomaly at the K-T boundary, and the Chicxulub crater is assumed to be the evidence for this impact. Of course, the association makes sense in theory. But the ground truth—the sedimentary and stratigraphic record—tells another story.

In reality, the most continuous K-T sections show a wide stratigraphic separation between the Chicxulub impact spherule ejecta layer and the K-T mass extinction and iridium anomaly, as for example in NE Mexico, Texas, and even the Chicxulub crater itself (Keller et al., 2003a, 2004a, 2004b, 2007, 2008). Nevertheless, the strong belief in the cause-and-effect scenario, termed the *strong expectation syndrome* by Tsujita (2001), has led some workers to ignore stratigraphic principles. This has resulted in a variety of imaginative interpretations linking Chicxulub impact spherules and the K-T mass extinction and iridium anomaly in a cause-and-effect scenario, including a giant impact-generated megatsunami, backwash and crater infill, large-scale regional slumping due to impact-induced earthquakes, and even injection of layered sediments over wide regions by massive earthquakes (e.g., Smit et al., 1992, 1996, 2004; Smit, 1999; Soria et al., 2001; Lawton et al., 2005; Schulte et al., 2006, 2008). Others found support for a cause-and-effect scenario in a few deep-sea sections of the Caribbean where the Chicxulub spherule ejecta layer and the K-T mass extinction are in close stratigraphic proximity, though associated with disturbed sediments, erosion, and condensed sedimentation (e.g., Sigurdsson et al., 1997; Norris et al., 1999, 2000; Klaus et al., 2000; MacLeod et al., 2006). In effect, interpretations are frequently driven by the *strong expectation syndrome* that any sediments between the K-T boundary and impact ejecta layers must be related to the Chicxulub impact.

This is unfortunate. Impacts are in fact invaluable stratigraphic tools when used within the context of stratigraphy and biostratigraphy. In theory, they provide an instantaneous time horizon in a rock sequence and are correlatable, wherever the particular impact ejecta layer can be found. This study evaluates impact signals in stratigraphy, their application, pitfalls and potential with respect to the K-T boundary and Chicxulub impact events. It addresses the reliability of impact signals as age markers, the problems of reworked impact ejecta, the continuity and completeness of the stratigraphic record, and the necessity of integrating impact signals into the bio-, chemo-, and isotope stratigraphic records. Examples are drawn from all areas with reported impact ejecta, including Texas, Mexico, Haiti, Cuba, Central America, and the deep sea (Fig. 1).

IMPACT STRATIGRAPHY

Impacts occurred throughout Earth's history with some regularity—small and large impacts, isolated or in clusters—and most do not coincide with mass extinctions (Fig. 2). Thus, impacts are not unique by themselves, nor do they generally cause mass extinctions, but they leave unique impact signals that vary from iridium anomalies to shocked minerals, Ni-rich spinels, glass spherules, shatter cones, and suevite breccias. Impacts vary in the signals they leave behind, but most signals are unsuitable as stratigraphic markers because of their sporadic occurrences and limited distributions.

Although frequently ignored, impacts may come in clusters over a period of as little as a couple of hundred thousand years (Napier, 2001, 2006), as notably documented for the late Eocene (Keller et al., 1983; Montanari and Koeberl, 2000; Poag et al., 2002; Harris et al., 2004), K-T boundary (Kelley and Gurov, 2002; Stewart and Allen, 2002; Keller et al., 2003a),

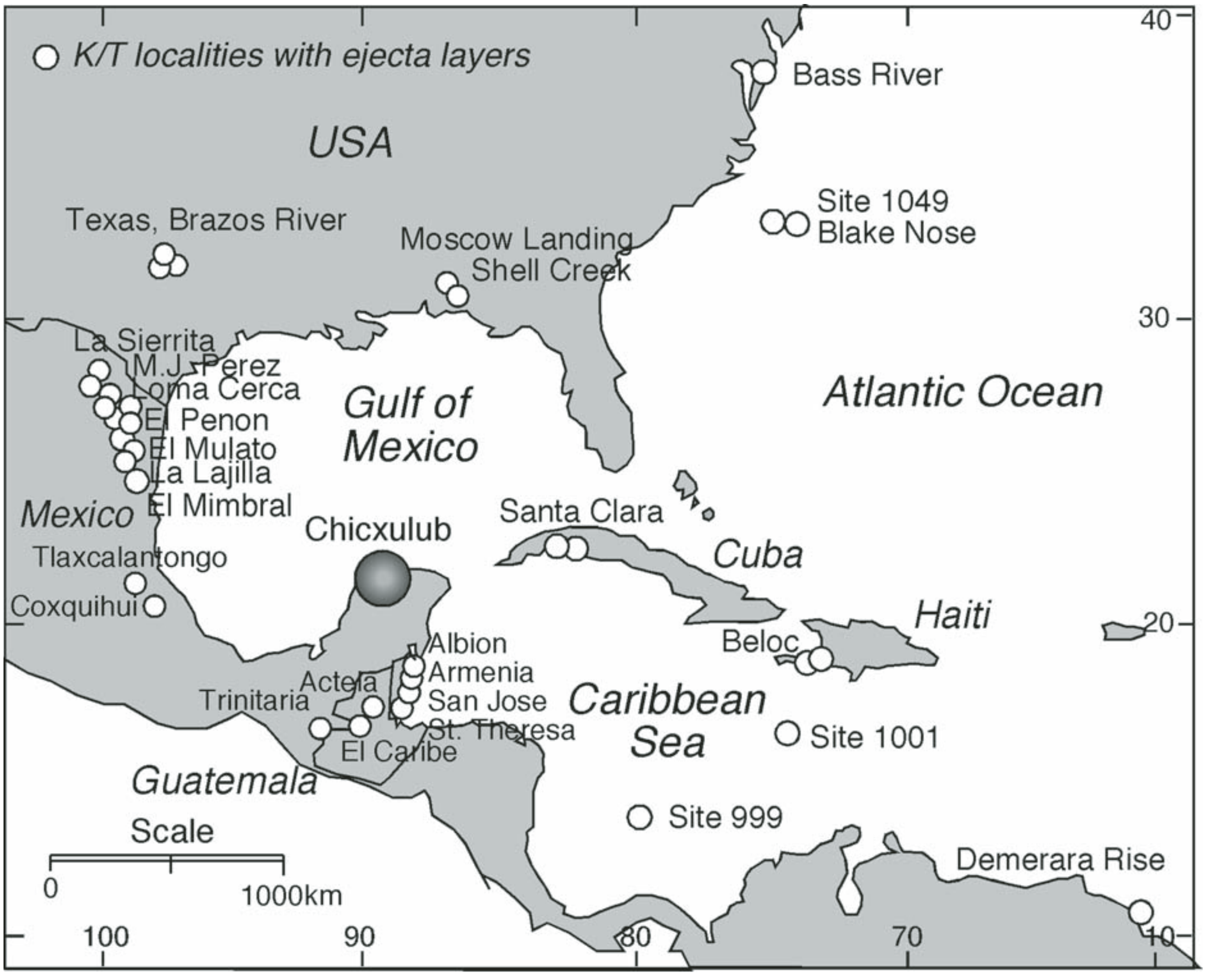


Figure 1. Locations of K-T sequences with Chicxulub impact spherule ejecta in the southern United States, Central America, and Caribbean.

Late Devonian (Glikson and Haines, 2005; Ma and Bai, 2002; Keller, 2005), and Precambrian (Glikson et al., 2004). Therefore, impact signals in close stratigraphic proximity cannot be assumed to represent one and the same impact event. This was first demonstrated by Keller et al. (1983) for the late Eocene and later confirmed by many studies (review in Montanari and Koeberl, 2000). The separation of impact signals in close stratigraphic proximity is therefore an opportunity to decipher the historical record and evaluate biotic consequences. *This is the promise and potential value of impact stratigraphy.*

Impact stratigraphy is part of event stratigraphy that incorporates unique short-term historical events, which leave signals in the sedimentary rocks, into a comprehensive scheme of relative age from oldest to youngest in any given rock sequence. The sedimentary and fossil records before and after the impact signal yield the clues to the environment. Although this seems like a straightforward application, in fact it is complicated by the particular sedimentary environment and the completeness of the sedimentary records. For example, impact signals that are well separated in high-sedimentation marginal shelf environments are frequently juxtaposed in condensed sequences of the deep sea (e.g., Bass River, Blake Nose, Demerara Rise). Hiatuses may have removed sediments containing the impact signals, and erosion and redeposition of impact ejecta into younger sediments results in disparate age relationships (e.g., Mexico, Haiti, Belize, Guatemala). Stratigraphy and biostratigraphy are the primary tools that can unravel the complex postdepositional history of the sedimentary record. But to do so, high-resolution biostratigraphy is necessary.

High-Resolution K-T Biostratigraphy

Planktic foraminifera provide excellent biomarkers for the K-T boundary transition because they suffered the most severe mass extinction of all microfossil groups. All tropical and subtropical specialized large species (2/3 of the assemblage) died out at or shortly before and after the K-T boundary, and their extinction was followed by the rapid evolution and diversification of Danian species beginning within a few centimeters of the boundary clay and Ir anomaly in most sequences. Critical biomarkers

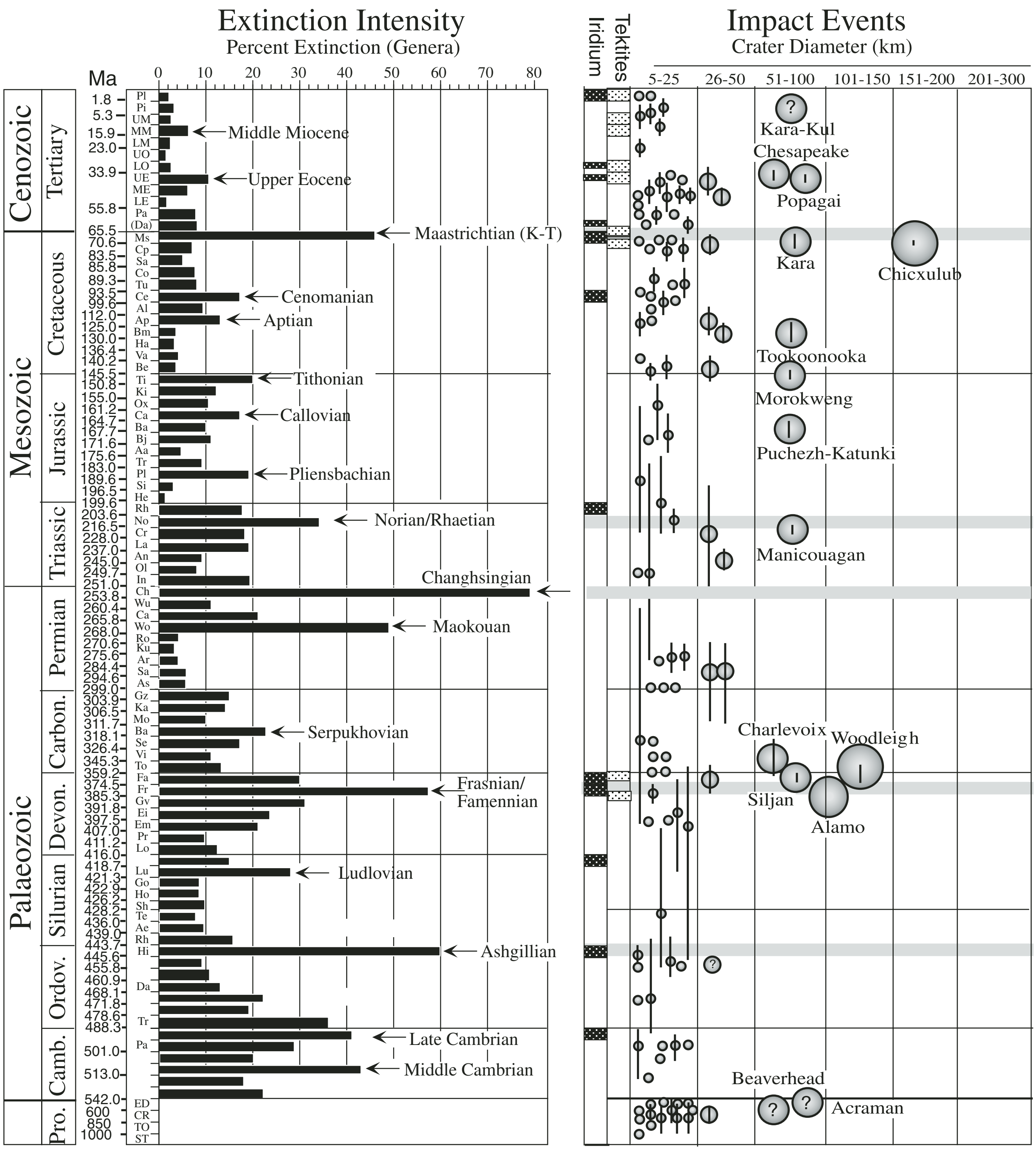


Figure 2. Mass extinctions and impacts during the Phanerozoic. Stratigraphic subdivisions and numerical ages from the 2004 International Commission of Stratigraphy Chart of Gradstein and Ogg (2004). The extinction record is based on genus-level data by Sepkoski (1996) and follows an earlier compilation by MacLeod (1998, 2003), with some modification based on Hallam and Wignall (1997). The number of impact events and the size and age of craters follows largely the Earth Impact Database (Grieve, 2005). Modified after Keller, 2005.

for the K-T boundary clay zone P0 include the first appearances of *Parvularugoglobigerina extensa*, *Globoconusa daubjergensis*, *Eoglobigerina eobulloides*, and *Woodringina hornerstownensis* (Fig. 3). The first appearances of *P. eugubina* and/or *P. longiapertura* mark the base of zone P1a, which spans the range of these species. Subdivision of this zone into P1a(1) and P1a(2) based on the first appearances of *Subbotina triloculinoides* and *Parasubbotina pseudobulloides* provides an important additional age control for the early Danian (Keller et al., 1995, 2002a). Below the K-T boundary, the most important biomarker is the range of *Plummerita hantkeninoides*, which marks zone CF1 and spans the last 300 k.y. of the Maastrichtian (Pardo et al., 1996). Ages for these biozones are estimated based on paleomagnetic stratigraphy, radiometric dates, and extrapolation based on average sediment accumulation rates (Fig. 3). In this study, the stratigraphic evaluation of Chicxulub impact markers uses the Danian zonation of Keller et al. (1995, 2002a) and the Maastrichtian zonation of Li and Keller (1998a) because they provide higher-resolution age control compared with the zonal scheme of Berggren et al. (1995) and Caron (1985).

Defining the K-T Boundary

The El Kef section of Tunisia was officially designated the Cretaceous-Tertiary (K-T) boundary global stratotype section and point (GSSP) at the International Geological Congress in Washington, D.C., in 1989. The official definition of the K-T boundary was never published but was summarized in Keller et al. (1995). The K-T boundary was defined based on (1) a major lithological change from carbonate-rich Maastrichtian sediments to a black organic-rich clay layer, called the "boundary clay," with a thin, 3–4 mm oxidized red layer at the base, (2) an iridium anomaly largely concentrated in the red layer, (3) the mass extinction in marine plankton, particularly the extinction of all tropical and subtropical planktic foraminiferal species nearly coincident with the base of the clay layer, (4) the first appearance of Danian species

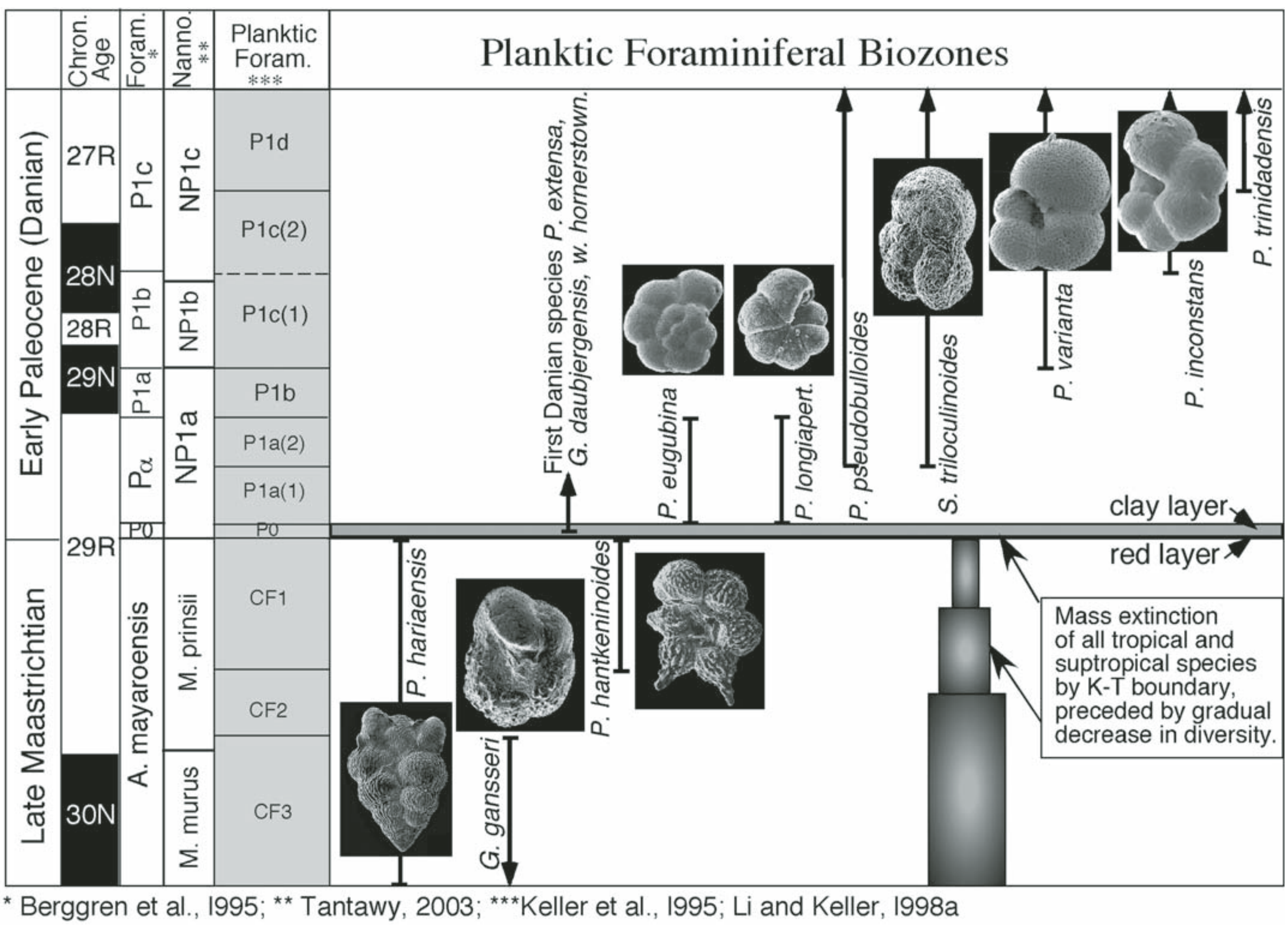


Figure 3. High-resolution planktic foraminiferal biozonation for the Cretaceous-Tertiary transition used in the stratigraphic analysis of impact ejecta deposits. Note that this biozonation significantly refines the resolution for the late Maastrichtian zonal scheme by replacing the upper *A. mayaroensis* zone by three biozones and by subdividing the *P. eugubina* zone P1a into two subzones based on the first appearances of *P. pseudobulloides* and *S. triloculinoides*. Modified after Keller et al., 2003a.

immediately (~1–5 cm) above the extinction horizon, and (5) a 2‰–3‰ negative shift in $\delta^{13}C$ values of marine carbonate (Keller et al., 1995) (Fig. 4). All five have remained remarkably consistent K-T boundary markers in marine sequences worldwide.

Gradstein and Ogg (2004; Molina et al., 2006) recently introduced a K-T boundary definition that reduced these identifying criteria to just the "Ir anomaly associated with a major extinction horizon" (see International Commission on Stratigraphy Web site on GSSPs). This is unfortunate because anomalous Ir concentrations are not unique to the K-T boundary, or may be absent in K-T sediments, whereas the extinction horizon is minor in many microfossils and macrofossils (e.g., palynomorphs, diatoms, radiolarian, benthic foraminifera, ostracods, ammonites, bivalves, see review in Keller, 2001; MacLeod, 1998) and highly reduced in shallow-water environments (e.g., planktic and benthic foraminifera, nannofossils) (Méon, 1990; Keller, 1989; Tantawy, 2003; Culver, 2003). The best results are thus obtained by using all five criteria. But where this is not possible, the shift in $\delta^{13}C$ values of marine carbonate is a unique global oceanographic marker for the K-T boundary and mass extinction horizon, and the first appearance of Tertiary species relative to the $\delta^{13}C$ and the K-T boundary clay appears isochronous globally in shallow or deep environments.

IMPACT MARKERS

Impact signals are the boutique markers of stratigraphy—exquisite but rare to find. Out of a variety of potential impact markers, including iridium and other PGE (platinum group elements) anomalies, impact glass spherules, shocked minerals, Ni-rich spinels, shatter cones, suevite breccia, and impact tsunami deposits, only the Ir anomaly and Chicxulub impact spherules are in practice widespread reliable stratigraphic impact markers. Most other impact signals are at this time unsuitable because of their sporadic occurrences, disputed origins, and limited distributions.

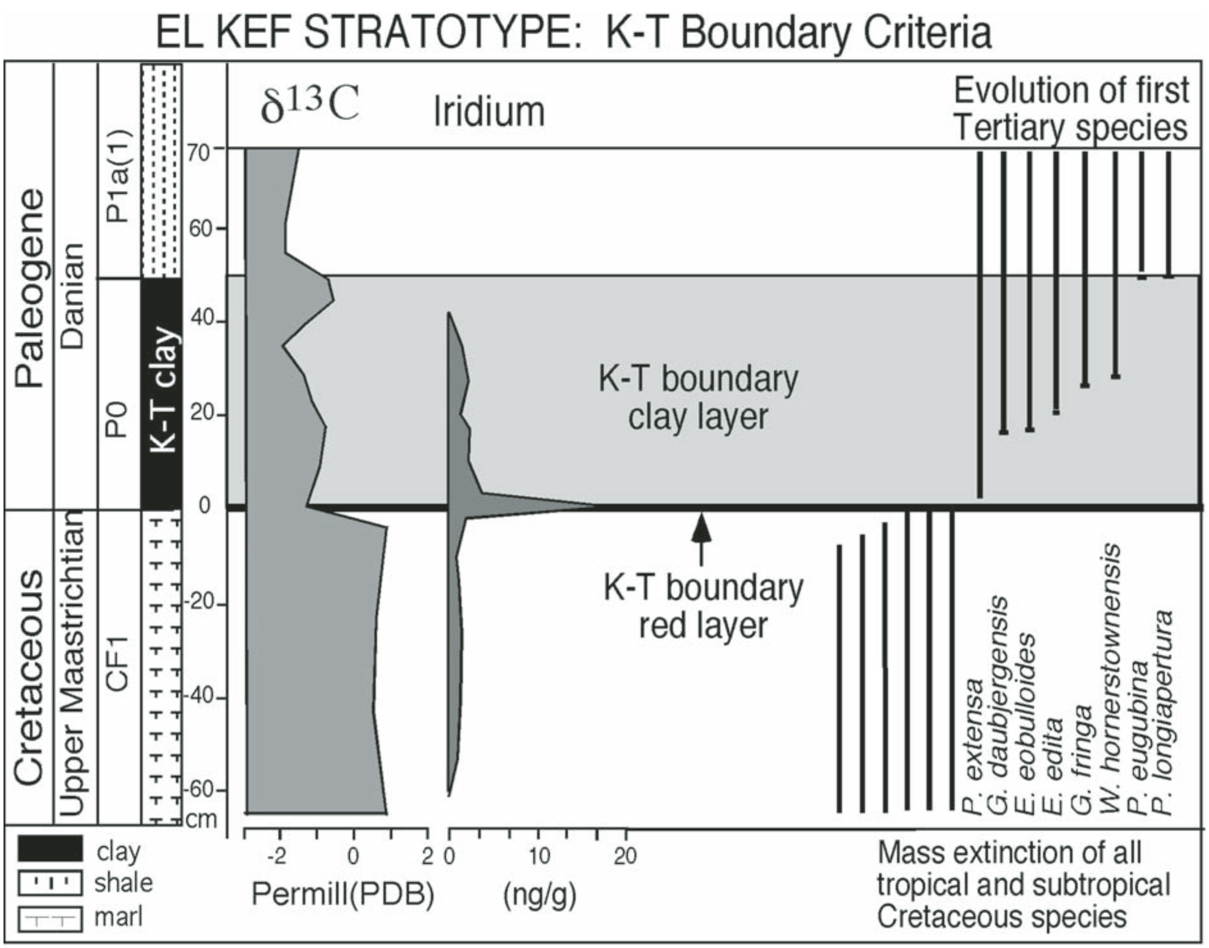


Figure 4. K-T boundary-defining criteria based on the El Kef stratotype. The K-T boundary is defined by (1) the mass extinction of tropical and subtropical planktic foraminifera, (2) the first occurrence of Tertiary species, (3) the 2‰–3‰ drop in $\delta^{13}C$ values marking a global oceanographic change, (4) a lithological change from the carbonate-rich Cretaceous sediments to a dark organic-rich clay with a red oxidized layer at the base, and (5) anomalous concentrations of iridium and other PGEs in the red layer and/or boundary clay. Note that Chicxulub impact spherules are not present at El Kef and are not part of the K-T boundary-defining criteria. Modified after Keller et al., 1995.

Iridium

Stratigraphic Position of Iridium and the K-T Boundary

Anomalous concentrations of iridium were first discovered in the K-T boundary clay in Gubbio, Italy, and linked to an extraterrestrial impact by Alvarez et al. (1980). Since then the Ir anomaly has been identified worldwide in K-T clays, coincident with a 2‰–3‰ negative shift in $\delta^{13}C$ values, the mass extinction of planktic foraminifera, followed by the evolution of the first Danian species. All of these markers therefore have become key identifying criteria for the K-T boundary. As noted above, the K-T boundary is easily recognized in the field by the abrupt lithologic change from carbonate-rich Maastrichtian sediments to dark organic-rich clay that is commonly very thin (1–5 cm) with a thin, 2–4 mm red layer at the base that contains maximum Ir concentrations (Fig. 4). Today, the presence of an Ir anomaly in the K-T clay layer is generally considered as (1) key evidence for a meteorite impact, (2) that it occurred precisely at the K-T boundary, and (3) that the impact either caused or at least substantially contributed to the mass extinction. This rule of thumb has served well. However, some caution is in order because times of multiple impacts may produce multiple Ir anomalies (Fig. 2).

Iridium Anomaly in Early Danian Zone P1a

A little-noticed second Ir anomaly has been observed in the early Danian zone P1a (middle to upper part of the *P. eugubina* zone; Fig. 3). This Ir anomaly has been observed to date in Haiti, central Mexico (Coxquihui), southern Mexico (Bochil), and Guatemala (Keller et al., 2001, 2003a, 2003b; Stinnesbeck et al., 2002; Stüben et al., 2002, 2005), and also in the Indian Ocean ODP Site 752B (Michel et al., 1991). At Site 752B, the K-T Ir anomaly is large (~4 ppb), followed by a second Ir anomaly (2 ppb) 60 cm above it in the *P. eugubina* zone P1a (Keller, 1993). In the Beloc sections of Haiti the Ir anomaly is concentrated in a thin red layer above a 5 cm thick cross-bedded sandstone within subzone P1a(1) and well above the spherule deposit and K-T boundary (Fig. 5). The chondrite-normalized PGE pattern indicates a cosmic origin with higher Ir values compared to Pt and Pd (Stüben et

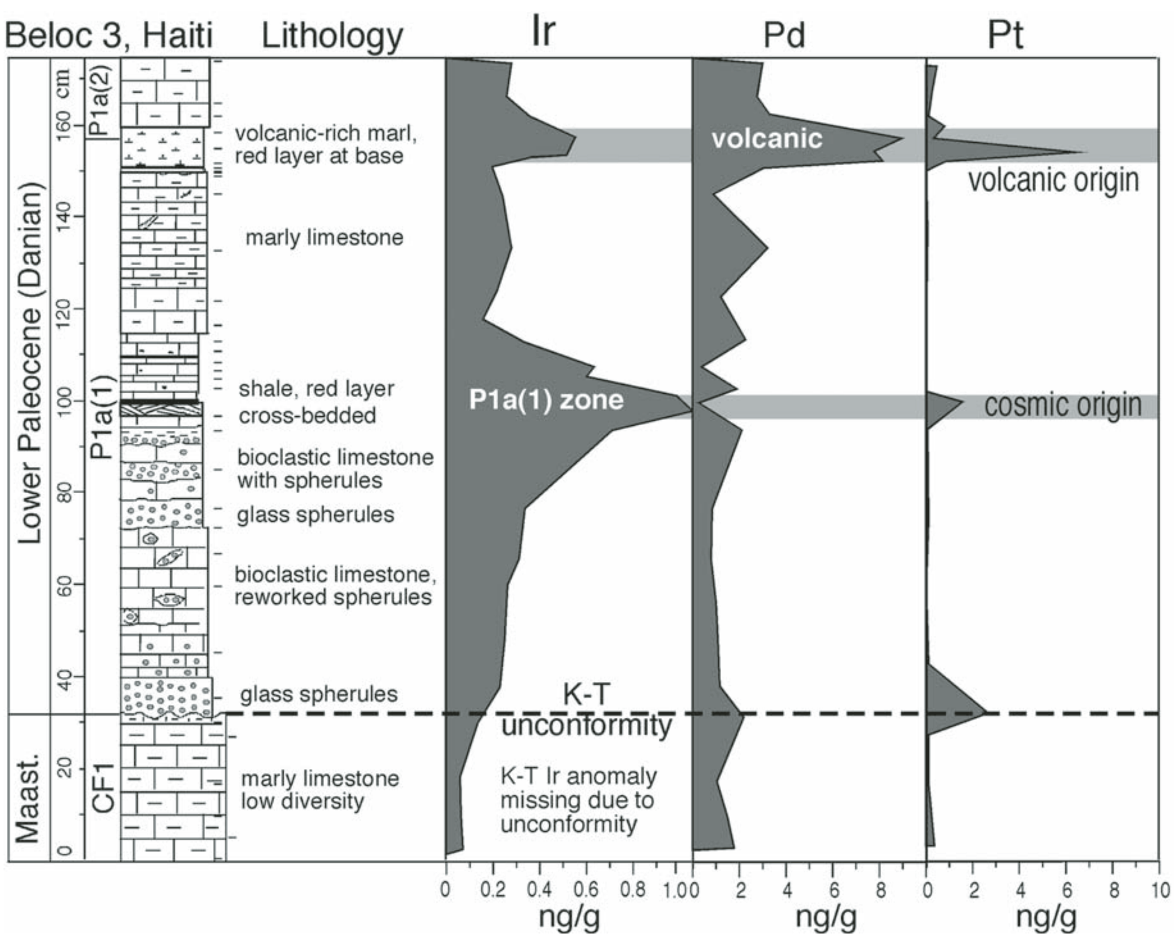


Figure 5. The K-T section of Beloc 3 in Haiti shows a lithological sequence with two PGE anomalies. The lower P1a(1) Ir anomaly is of cosmic origin, the upper small Ir and large Pd and Pt anomalies indicate a volcanic origin. The K-T boundary is missing due to erosion. Note that although the Haiti sections are stratigraphically nearly complete (e.g., all zones present except for the boundary clay), the Chicxulub spherules are reworked within early Danian sediments. Modified after Keller et al., 2001.

al., 2002). In the same section 50 cm higher up is a second PGE anomaly in a volcaniclastic layer with a basalt-like pattern (minor Ir [0.5 ng/g], major Pt and Pd enrichments [7.5 ng/g]) suggesting a volcanic source.

In Bochil, Chiapas (Mexico), the same pattern of cosmic and volcanic anomalies was observed (Keller et al., 2003a; Stüben et al., 2005) (Fig. 6), although the P1a(1) Ir anomaly is stratigraphically closer to the K-T boundary due to erosion of the lowermost Danian. This is indicated by the simultaneous and abundant first appearance of six Danian species (*Parvularugoglobigerina eugubina*, *P. longiapertura*, *P. extensa*, *Globoconusa daubjergensis*, *Woodringina hornerstownensis*, *Chiloguembelina midwayensis*). In Coxquihui, central Mexico, the K-T boundary is marked by a 2 cm spherule layer above a thin silty sandstone that abruptly terminates Maastrichtian marls of zone CF1 (Fig. 7). No Ir anomaly is present. Abundant Danian species indicative of subzone P1a(1) are present in the overlying 20 cm of clayey marl and mark a hiatus, with the boundary clay and lower part of P1a(1) missing (Stinnesbeck et al., 2002). A 60 cm thick spherule layer with abundant reworked Maastrichtian species overlies the clayey marl and indicates that this layer is reworked from Maastrichtian sediments. In the undisturbed marls above is an Ir and Pd anomaly of probable cosmic origin, which marks a Danian impact, similar to Bochil and Beloc.

Thus, multiple Ir and PGE anomalies of both cosmic and volcanic origins may be present in the early Danian, and these could be mistaken for the K-T Ir anomaly in condensed sequences. High-resolution biostratigraphic control is therefore vital to determine the continuity of the sedimentation record and identify the K-T Ir anomaly. A detailed investigation of Ir concentrations and their stratigraphic positions at the K-T boundary, the early Danian, and late Maastrichtian zone CF1 is yet to be done.

Iridium Profiles

Iridium and other PGE anomalies have received much attention as indicators of extraterrestrial sources, such as asteroids, comets, cosmic dust, or impact ejecta. This has been justified on the basis that iridium is highly depleted in Earth's crust but enriched in some asteroids and comets and in Earth's interior, where it is brought to the surface by volcanic activity. Because it is assumed that iridium is extruded over a long time period and therefore likely distributed over broad low plateaus, a sharp peak in iridium concentrations is generally interpreted as a cosmic marker. However, a volcanic origin cannot be excluded because

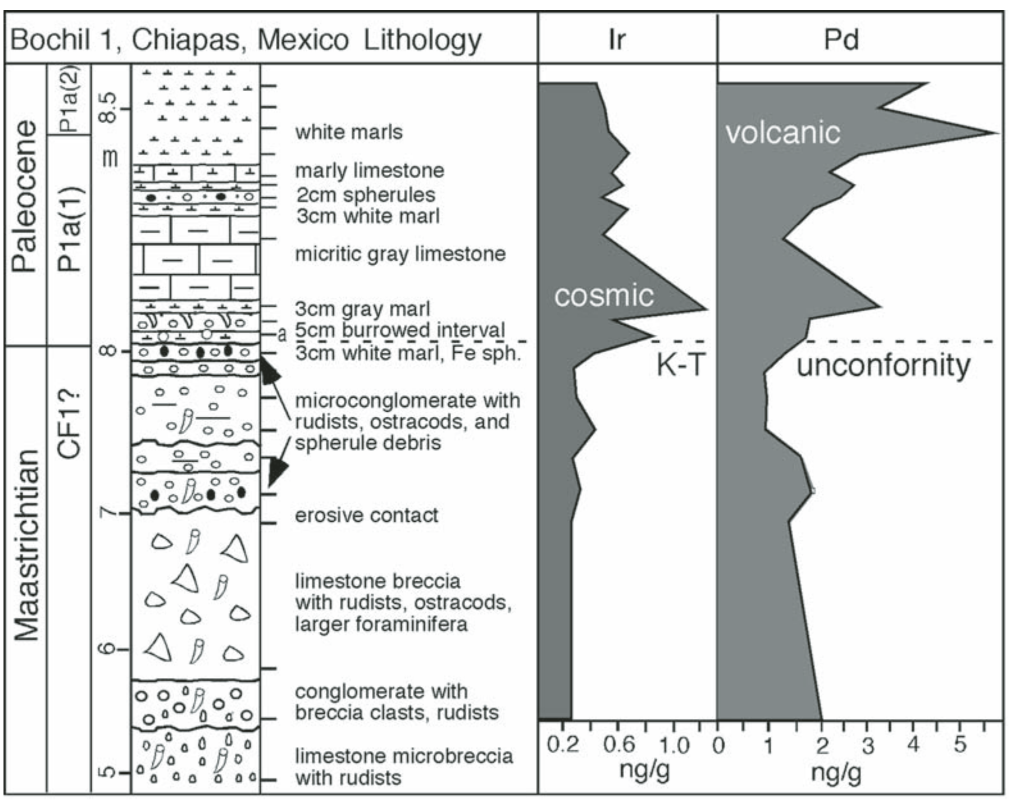


Figure 6. At Bochil 1 in Chiapas, Mexico, altered glass spherules are present at the base and top of a microconglomerate layer of probable latest Maastrichtian age. The first marl layer above this microconglomerate contains early Danian *P. eugubina* subzone P1a(1) planktic foraminifera, as well as Ir and Pd anomalies. A second Pd anomaly near the P1a(1)-P1a(2) boundary appears to be of volcanic origin, similar to Beloc, Haiti. Modified after Keller et al., 2003a.

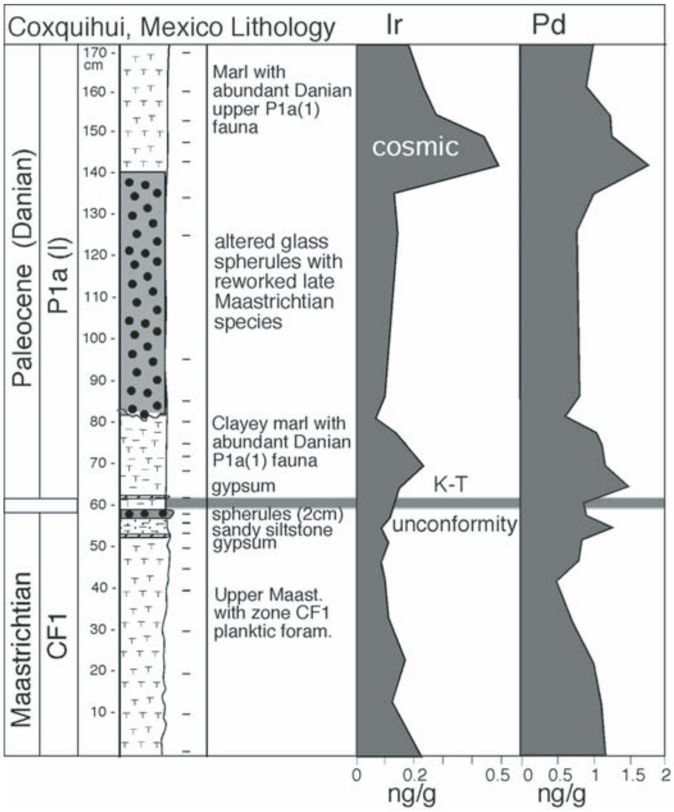


Figure 7. At Coxquihui in central Mexico, the K-T boundary is marked by an unconformity above a 2 cm thick spherule layer, which underlies Danian marls with an abundant P1a(1) assemblage. A 60 cm thick spherule-rich layer with abundant Maastrichtian species indicates redeposition of the Chicxulub spherule layer in the early Danian. The Ir anomaly above it appears to be of cosmic origin and correlates with similar anomalies in Bochil and Beloc. Modified after Stinnesbeck et al., 2002.

recent studies have shown that Deccan eruptions near the K-T boundary occurred rapidly (Chenet et al., 2007). Moreover, sharp peaks may also result from condensed sedimentation, which must be ruled out by normalizing to elements that are constantly present in sediments (e.g., Al or Ti). Ir concentrations at the K-T boundary typically are 1 ppb or more, but smaller 0.5–1.0 ppb concentrations are common. Even smaller concentrations (0.2–0.4 ppb) are generally suspect and should be interpreted with great caution, as they may result from a variety of terrestrial processes.

Sawlowicz (1993) discussed a host of processes that could be responsible for the K-T boundary Ir anomaly and other PGE concentrations. Although the original K-T Ir anomaly is generally considered extraterrestrial, postdepositional oxidation and reprecipitation is a major concern. The K-T red layer consists of thin iron oxide–stained laminae with common iron oxide spherules highly enriched in Ir and noble metals that probably resulted from oxidation of primary iron sulfides (Brooks et al., 1985). Oxidation within this red layer may have caused the degradation of PGE-rich organic compounds and precipitation of native metals and their alloys (Elliott et al., 1989). Such red oxidized layers are commonly found at lithologic boundaries. For example, in the Beloc sections of Haiti, the two early Danian zone P1a(1) Ir and PGE anomalies are each associated with thin red oxidized layers, one above a rippled sandstone and the other below a volcaniclastic layer (Fig. 5). A PGE anomaly may result from the removal of primary components, or in the case of the K-T red layer the addition of mineralizing solutions to a redox boundary. Sawlowicz (1993) concluded that the unusually high Ir concentration at the K-T boundary is probably the result of an extraterrestrial impact and complex terrestrial processes.

Remobilization at Redox Boundaries

Ir anomalies typically occur in organic-rich shales or clays, which serve as low-permeability redox boundaries, and are associated with sandstones or carbonates. In these sediments Ir can move both upward and downward at redox boundaries (Gilmore et al., 1984; Tredoux et al., 1988; Sawlowicz, 1993; Wang et al., 1993). This process may explain the minor (0.2–0.3 ppb) Ir enrichments within the sandstone complex at El Mimbral in NE Mexico and Brazos-1 in Texas. At El Mimbral I, the main Ir anomaly is in the basal Danian clay above the sandstone complex that infills a submarine channel and coincident with the abrupt and abundant first appearance of four Danian zone P1a(1) species (Keller et al., 1994a; Rocchia et al., 1996). Minor Ir enrichment occurs at the top of the underlying rippled calcareous sandstone (Fig. 8A). At El Mimbral II, located outside the submarine channel and ~100 m from El Mimbral I, the sandstone complex is reduced to the topmost 20–25 cm thick rippled sandy limestone. At this section, the Ir anomaly begins in the red layer, coincident with the first appearance of Danian zone P1a(1) species, and reaches maximum concentrations ~7 cm above (Fig. 8B) (Stinnesbeck et al., 1993; Keller et al., 1994a, 1994b). Similar to El Mimbral I, minor (0.2 ppb) Ir concentrations occur in the underlying rippled sandy limestone.

Similarly, at Brazos-1 (Texas) the main Ir anomaly is in a thin red-brown clay and 1 cm sand layer ~17–19 cm above the sandstone complex, as noted in three different studies (Ganapathy et al., 1981; Asaro et al., 1982; Rocchia et al., 1996). Two minor Ir enrichments occur in the sandstone complex below, just above the calcareous claystone horizon (CCH) and in the laminated sandstone layer above the hummocky sandstone (Fig. 9A). These minor enrichments are likely due to postdepositional processes discussed in Sawlowicz (1993). A photo of the Brazos-1 outcrop with the Ir data superimposed (Fig. 9B) illustrates the distinct lithologic separation of the main Ir anomaly and the top of the event deposit.

In Mexico and Texas the minor Ir enrichments in sandstones below the main Ir anomaly have been interpreted as evidence that the sandstone complex was generated by an impact tsunami (Smit et al., 1992, 1996; Hansen et al., 1993; Smit, 1999; Heymann et al., 1998; Schulte et al., 2006). In this scenario the main Ir anomaly is interpreted as fallout after deposition of the sandstone

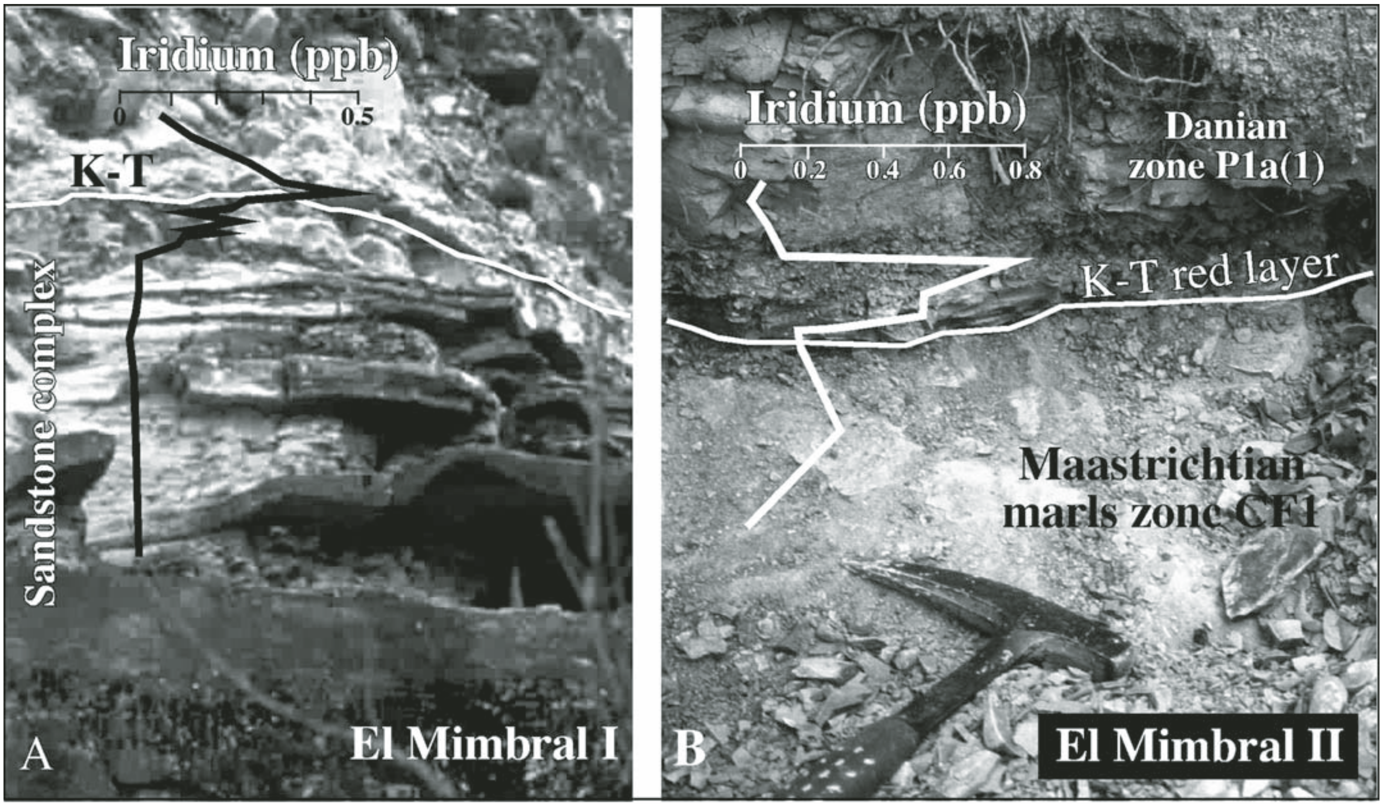


Figure 8. A: Ir anomaly from Mimbral I, superimposed over outcrop lithology from which it was measured (data from Rocchia et al., 1996). Note that only minor Ir concentrations occur in the topmost rippled sandy limestone of the sandstone complex, and the main anomaly is coincident with the abrupt and abundant appearance of Danian planktic foraminifera in the claystone above (Keller et al., 1994a). B: Ir anomaly from Mimbral II, measured ~100 m from Mimbral I where the sandstone complex consists only of the topmost 20–25 cm thick rippled sandstone. Note that the Ir anomaly begins in the K-T red layer above the rippled sandy limestone and reaches maximum values 7 cm above.

complex by a tsunami generated by the Chicxulub impact, an interpretation that ignores the presence of bioturbated horizons within the sandstone complex that indicates long-term deposition (Keller et al., 2003a, 2007; Gale, 2006). A more likely interpretation is postdepositional remobilization. The complex behavior of iridium and other PGEs in sedimentary environments is still poorly understood. Therefore, such small anomalies must be considered with caution and the sedimentary sequences interpreted based on the integration of geochemical, mineralogical, sedimentologic, and paleontologic data.

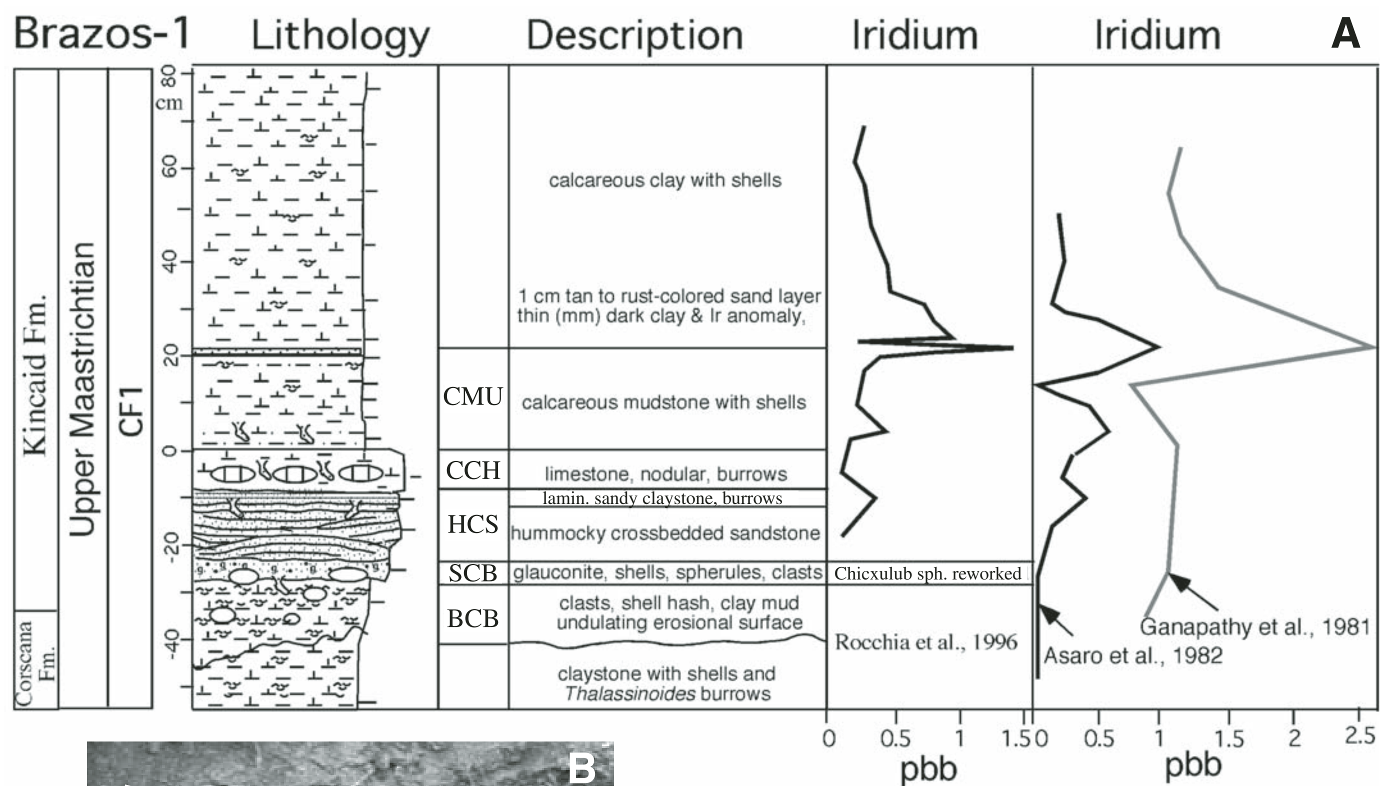
Iridium and Chicxulub Impact Spherules?

No iridium anomaly has ever been found in stratigraphic layers associated with Chicxulub impact ejecta, whether in the impact crater or spherule ejecta layers, in Texas, Mexico, Haiti, Belize, or Guatemala (Rocchia et al., 1996; Keller et al., 2003a; Schulte et al., 2003; Harting, 2004; Stüben et al., 2002, 2005). This suggests that the Chicxulub impact was a "dirty snowball"–type comet without iridium enrichment. However, close stratigraphic proximity of an Ir anomaly and Chicxulub impact spherules in some terrestrial and deep-sea sections is frequently cited as unequivocal evidence that the Chicxulub impact is of K-T age (e.g., Norris et al., 1999, 2000; MacLeod et al., 2006; Morgan et al., 2006). These claims are examined below.

IMPACT SPHERULES

K-T Boundary Spherules—Not Chicxulub Origin

Several hundred K-T boundary sequences have been studied to date around the world, and most complete sedimentary records share the same characteristics: an organic-rich boundary clay with a thin red layer at the base, iridium and other PGE anomalies usually concentrated within the red layer, a negative shift in $\delta^{13}C$ (though not in high latitudes; Barrera and Keller, 1994), and the mass extinction of Cretaceous species and evolution of Tertiary species (Fig. 4). In all these sequences only two types of spherules are common: (1) the tiny iron oxide spherules, which mostly occur in encrusting clusters or singly in the red layer or K-T clay; these are highly enriched in Ir and noble metals that may have resulted from oxidation of primary iron sulfides (Brooks et al., 1985); and (2) pyrite framboids, which are very common in the organic-rich clay and are indicative of low-oxygen conditions (Wignall et al., 2005).



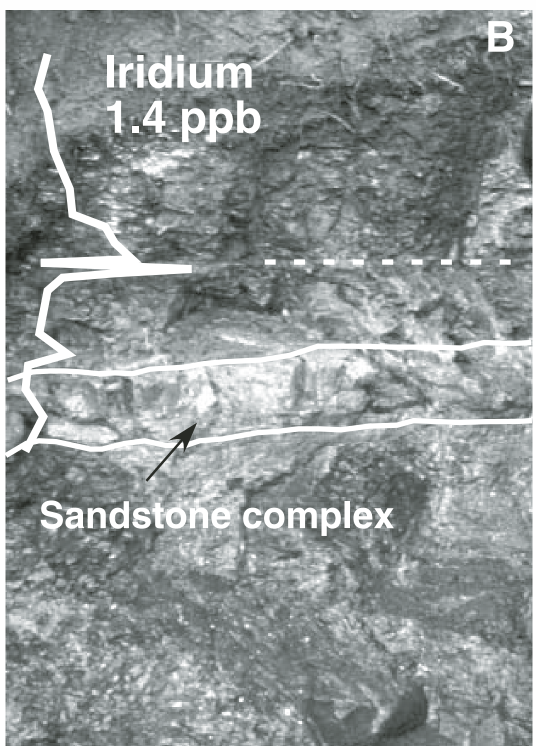


Figure 9. A: At the classical Brazos-1 riverbank section near the Route 413 bridge across the Brazos River, three Ir studies found the anomaly in a thin red-brown layer and 1 cm sandstone 17–19 cm above the top of the calcareous claystone horizon (CCH) that forms the top of the event deposit. The two minor Ir enrichments just above the CCH within a laminated sandy claystone are likely due to postdepositional processes. Unit labels from Yancey (1996). BCB—basal conglomerate bed; SCB—spherulitic conglomerate bed; HCS—hummocky sandstone unit; CCH—calcareous clayey horizon; CMU—calcareous mudstone unit. B: Photo of the K-T boundary and Ir anomaly at Brazos-1. Note that the minor Ir enrichment above the calcareous claystone horizon (CCH) is likely the result of postdepositional processes. Ir data from Rocchia et al. (1996). Photo courtesy of T. Yancey.

A few sections contain rare clay spherules of ~1–2 mm in size, often compressed and iron-coated (e.g., Spain [Agost], Tunisia [El Kef and Elles], Israel [Mishor Rotem]). Smit (1999) interpreted these K-T clay spherules as altered Chicxulub impact glass, although they largely consist of glauconite clay. These spherules are unlike the clay-altered glass spherules characteristic of the Chicxulub impact with their internal calcite-filled air bubbles, and the glass alteration product is a Cheto- or Mg-smectite clay, rather than glauconite (Keller et al., 2003a, 2003b, 2004a, 2004b, 2007, 2008). No relic impact glass has ever been detected in the K-T clay, and the clay content is unlike any altered Chicxulub impact glass. Even in Mexico, no Chicxulub impact spherules occur in the K-T red layer and boundary clay (e.g., La Sierrita, La Parida, El Mimbral)—but they are abundantly present below the sandstone complex, which is well below the K-T boundary, as well as in early Danian sediments above the K-T boundary (e.g., Haiti, Belize, Guatemala). At this time, the rare K-T clay spherules largely appear to be of normal sedimentary origins, though detailed mineralogical and geochemical studies have yet to be done to compare them to the Chicxulub impact glass spherules.

Chicxulub Impact Glass Spherules

Chicxulub impact spherules are almost always spherical or compressed oval, range in size from 1 to 5 mm, and generally contain multiple air cavities as seen in thin sections (Fig. 10). Relic glass, and sometimes well-preserved glass spherules and glass shards can be found in cemented spherule rocks. Spherules that have been eroded and redeposited generally contain a matrix rich in clasts, clastic minerals (Fig. 10A–C), and shallow-water debris (wood, plants, shallow-water foraminifera; Smit et al., 1992; Keller et al., 1994a). In contrast, spherules and glass shards from the original ejecta layer are cemented by a calcite matrix and may show concave-convex contacts that indicate deposition while still malleable (Fig. 10D–F) or postdepositional compression alteration. The spherule glass is mostly altered to green clay (Mg-smectite) with only relic glass preserved. Nevertheless, in outcrops the spherulitic texture is preserved because calcite infills air cavities (Fig. 11). When these samples are washed in the laboratory the green clay frequently dissolves, leaving the white calcite spheres. Throughout Central America, the Caribbean, around the Gulf of Mexico, southern United States, and New Jersey, these spherules have the same physical and chemical characteristics. They are linked to the Chicxulub impact based on their geographic distribution, $^{39}Ar/^{40}Ar$ ages close to the K-T boundary (Sigurdsson et al., 1991; Swisher et al., 1992; Dalrymple et al., 1993), and chemical similarity to Chicxulub melt rock (Izett et al., 1991; Blum et al., 1993; Koeberl et al., 1994; Chaussidon et al., 1996; Schulte et al., 2003; Harting, 2004).

Stratigraphic Position of Spherule Deposits

Chicxulub impact spherules are excellent stratigraphic markers in Central America, around the Gulf of Mexico, and in Texas (Fig. 1), where they are relatively easy to spot in outcrops by their coarse-grained spherulitic texture and green color (Fig. 11). They have never been observed in the K-T boundary clay, red layer, and Ir anomaly. Most studies of the 1990s describe spherule deposits in NE Mexico ranging from 5 cm to 2 m thick and directly underlying a sandstone complex consisting of 1–3 m of sandstone followed by 1–2 m of alternating sand-silt-marl layers (Figs. 8A and 8B). These sandstone complexes are commonly interpreted as impact tsunami deposits because of their stratigraphic proximity

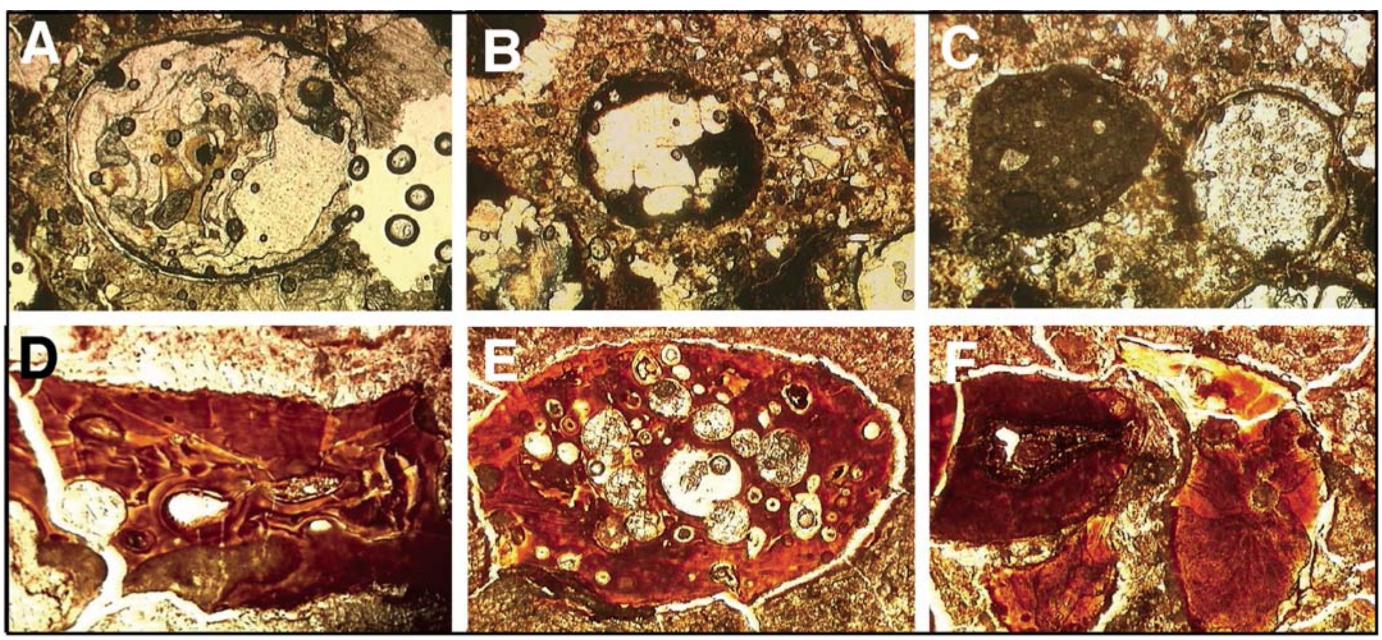


Figure 10. Chicxulub impact spherules from El Peñon, Mexico, as seen in thin sections. A–C: Spherules from the base of the sandstone complex have a matrix of clastic grains, clasts, and shallow-water foraminifera that indicate erosion from shallow areas and transport and redeposition in submarine canyons. D–F: Spherules and shards from the original spherule ejecta layer, ~4 m below the sandstone complex, are embedded in a matrix of calcite cement, which contains no shallow-water debris or clastic grains. Spherules are mostly spherical and range from 2 to 4 mm in size. Most spherules and glass shards contain multiple air cavities, which is characteristic of Chicxulub impact glass. The cavities are generally infilled with diagenetic calcite and the glass altered to Mg-smectite.

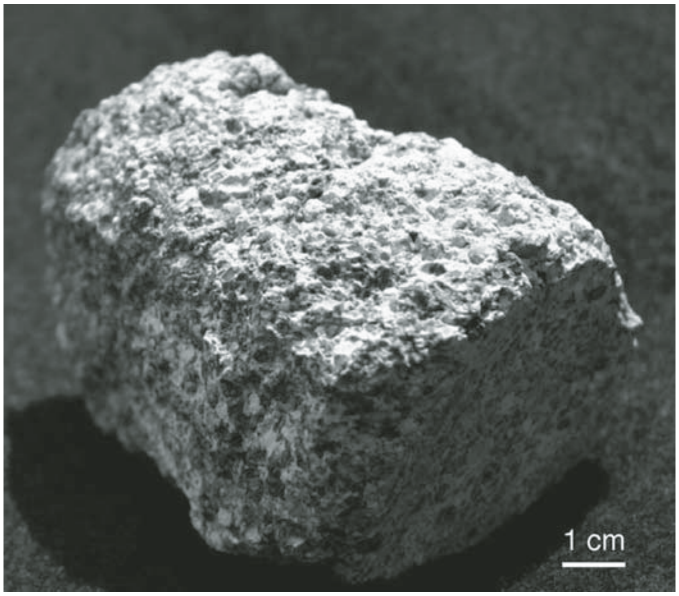


Figure 11. Chicxulub impact spherule rock from El Peñon, NE Mexico. Note that the spherulitic texture is largely preserved due to the diagenetic calcite that infills the spherule cavities. Its green color is largely due to glass alteration.

to the overlying K-T boundary (reviews in Smit, 1999; Keller et al., 2003a, 2003b). They infill submarine canyons, as indicated by their lenticular bodies of 100–300 m lateral extent. Laterally, the spherule unit disappears first, followed by the sandstone and finally the topmost calcareous rippled sandstone (see descriptions in Keller et al., 1994b; Stinnesbeck et al., 1996; Smit, 1999). The topmost rippled sandstone unit disappears last and is overlain by the K-T boundary clay, red layer, and Ir anomaly (e.g., El Mimbral, La Parida, La Sierrita) (Keller et al., 1994a; Lopez-Oliva and Keller, 1996; Stinnesbeck et al., 1996). No Chicxulub spherules have been observed in any K-T boundary clay layers in Mexico.

In the late 1990s a group of M.A. and Ph.D. students from Princeton and the Universities of Neuchatel, Switzerland, and Karlsruhe, Germany, undertook detailed field and laboratory investigations of the spherule and sandstone deposits and the underlying Maastrichtian sediments over a 50 km^2 area in NE Mexico (Lopez-Oliva and Keller, 1996; Lindenmaier, 1999; Schulte, 1999, 2003; Schilli, 2000; Affolter, 2000; Harting, 2004). Their studies documented over 45 K-T sequences, many of them with additional spherule layers in pelagic marls of the upper Maastrichtian, and the stratigraphically lowermost spherule layer up to 9 m below the sandstone complex (Fig. 12) (Keller et al., 2002b). This complex stratigraphic distribution of spherule

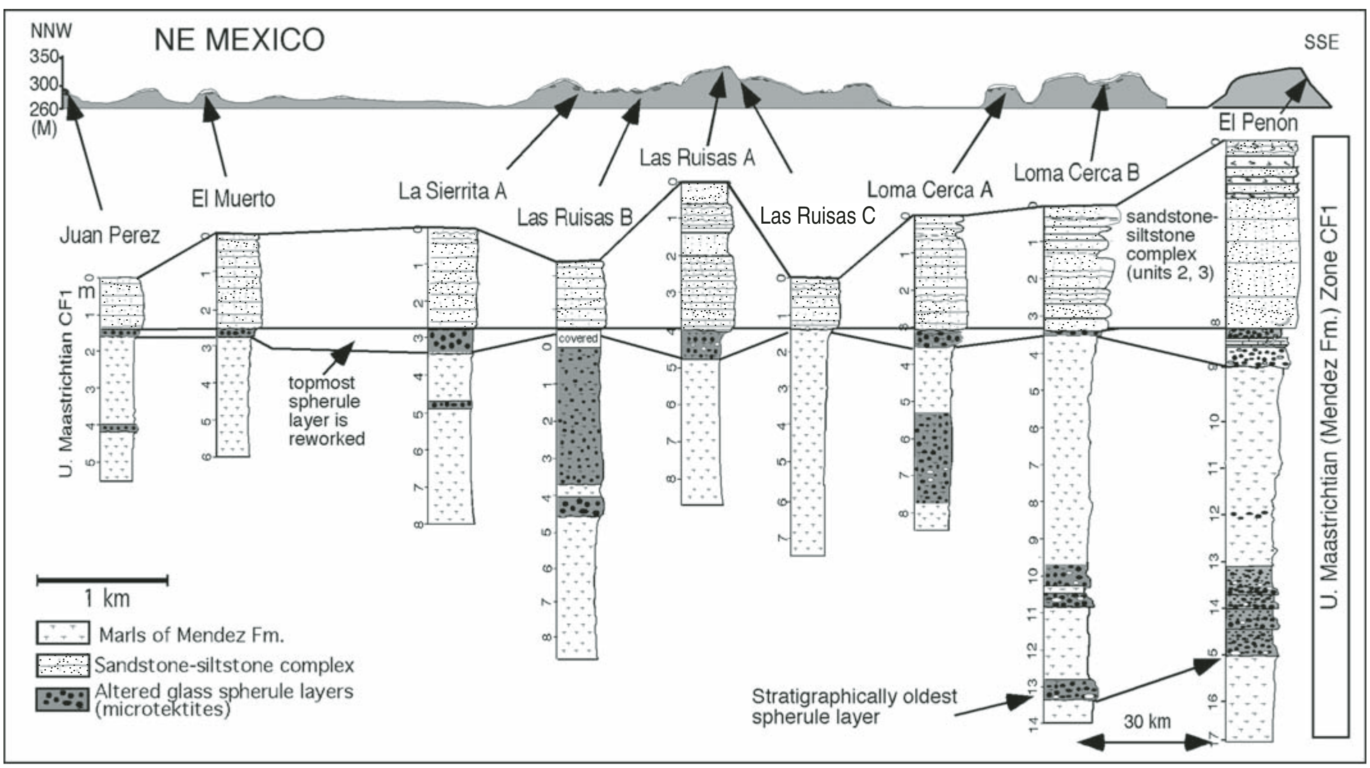


Figure 12. Stratigraphic and lithologic correlation of late Maastrichtian NE Mexico sections with sandstone complexes and altered Chicxulub impact spherule layers from Mesa Juan Perez to Mesa Loma Cerca (~8 km) and El Peñon (~30 km from Mesa Loma Cerca; Fig. 1). The siliciclastic deposits of units 2 and 3 form the top of the mesas as shown by the topographic relief, and the overlying sediments are eroded. In this area, all spherule deposits are within the Maastrichtian marls of the Mendez Formation and within zone CF1, which spans the last 300 k.y. of the Maastrichtian. Modified after Keller et al., 2002b, scale added.

ejecta in upper Maastrichtian sediments suggests a complex post-depositional history of erosion, transport, and redeposition. Thus, an impact ejecta layer cannot be assumed to be the impact time horizon without careful stratigraphic, biostratigraphic, and lithologic examinations of sediments above and below.

Reworked Spherules + Sandstone Complex = Tsunami?

NE Mexico

The most prominent stratigraphic features in K-T sequences of NE Mexico and Texas are thick sandstone complexes with Chicxulub impact glass spherules at the base (Fig. 12). These sandstone deposits underlie the K-T boundary and Ir anomaly. Because of the stratigraphic proximity of the sandstone deposits to the K-T boundary, they have been commonly interpreted as impact-generated tsunami deposits (e.g., Smit et al., 1992, 1996; Smit, 1999; Soria et al., 2001). This hypothesis has not held up under scrutiny and has been the topic of significant controversy. Even before the discovery of the stratigraphically older spherule deposits in upper Maastrichtian sediments, evidence indicated that rapid tsunami deposition was not likely. For example, burrows were first discovered at El Mimbral in the alternating sand, silt, and marl layers by Toni Ekdale during the 1994 NASA-LPI-sponsored field trip (led by Stinnesbeck, Keller, and Adatte) and subsequently documented as discrete burrowing horizons (*Thalassinoides*, *Chondrites*, J-shaped burrows; Fig. 13) in most sections of NE Mexico. These burrowing horizons suggest repeated colonization of the ocean floor during deposition (Keller et al., 1997, 2003a; Ekdale and Stinnesbeck, 1998). In addition, alternating coarse and fine-grained deposition and two volcanic ash (zeolite) layers indicate interrupted deposition over an extended time period (Adatte et al., 1996; Stinnesbeck et al., 1996).

The spherule layer at the base of the sandstone complex yielded further evidence of long-term deposition. In various sequences, most prominently at El Mimbral and El Peñon, a 20-cm-thick sandy limestone with rare spherule-infilled J-shaped burrows separates the spherules below the sandstone into two layers (Fig. 13). This indicates two spherule depositional events separated by sufficient time to deposit the sandy limestone and permit burrowing by marine invertebrates prior to deposition of the second spherule layer. The spherule deposits contain shallow-water debris, including a matrix of sand, clasts, foraminifera, wood, and leaves, transported from nearshore areas and carried by currents downslope to

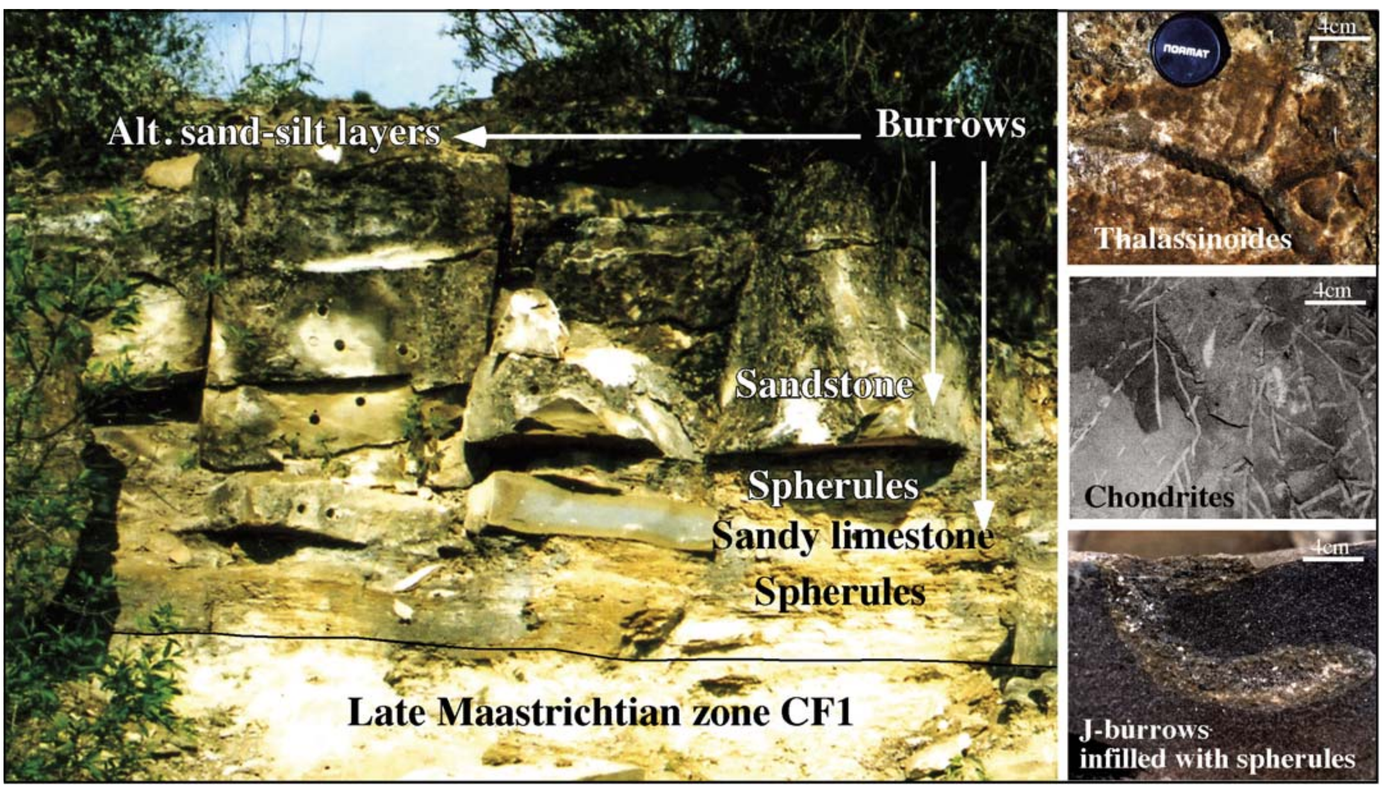


Figure 13. The sandstone complex at El Peñon, NE Mexico, overlies two reworked spherule layers that are separated by a 20 cm thick sandy limestone. J-shaped burrows infilled with spherules and truncated at the top are present in the limestone and overlying sandstone. Siltstone and marly layers above the sandstone are intensely burrowed by *Chondrites* and *Thalassinoides*. These are not characteristics that would be found in a tsunami deposit, but rather indicate deposition over an extended time period during which the ocean floor was repeatedly colonized by invertebrates. The K-T boundary is eroded at the top of the section.

their resting place at 500–1000 m depths (Keller et al., 1994a; Alegret et al., 2001). These spherules are thus reworked, transported, and redeposited—they do not represent the original Chicxulub ejecta fallout. These data are difficult if not impossible to reconcile with a tsunami interpretation, even without the discovery of the original spherule ejecta deposit in the underlying undisturbed upper Maastrichtian sediments (discussed below).

Texas, USA

In Texas, along the Brazos River of Falls County and its tributaries, Cottonmouth and Darting Minnow Creeks, the sandstone complex that underlies the K-T boundary and Ir anomaly is well developed and up to 2 m thick. These deposits have also been interpreted as of impact tsunami origin (Hansen et al., 1987; Bourgeois et al., 1988; Smit, 1999; Heymann et al., 1998; Schulte et al., 2006, 2008). As in Mexico, this interpretation is controversial and has not held up under scrutiny.

Yancey (1996) described the units of the sandstone complex from the base upward as basal conglomerate, a spherule-rich conglomerate with glauconite, clasts, phosphate and shell hash, a hummocky cross-bedded sandstone, rippled and laminated sandstones, and a calcareous mudstone at the top. He suggested the term "event deposits" for this sandstone complex, though in this study, as in NE Mexico, we will keep the term "sandstone complex" to describe these deposits. Gale (2006) and Keller et al. (2007, 2008) suggested that the stratigraphic discontinuities, multiple burrowed horizons, and alternating low- and high-energy depositional regimes of these deposits suggest seasonal storms, rather than an impact tsunami, and deposition during a low sea level.

An excellent sandstone complex was recovered in the recently drilled new core Mullinax-1, drilled near the classic Brazos-1 section. In this core, the spherules at the base of the sandstone deposit show three upward-fining units rich in impact

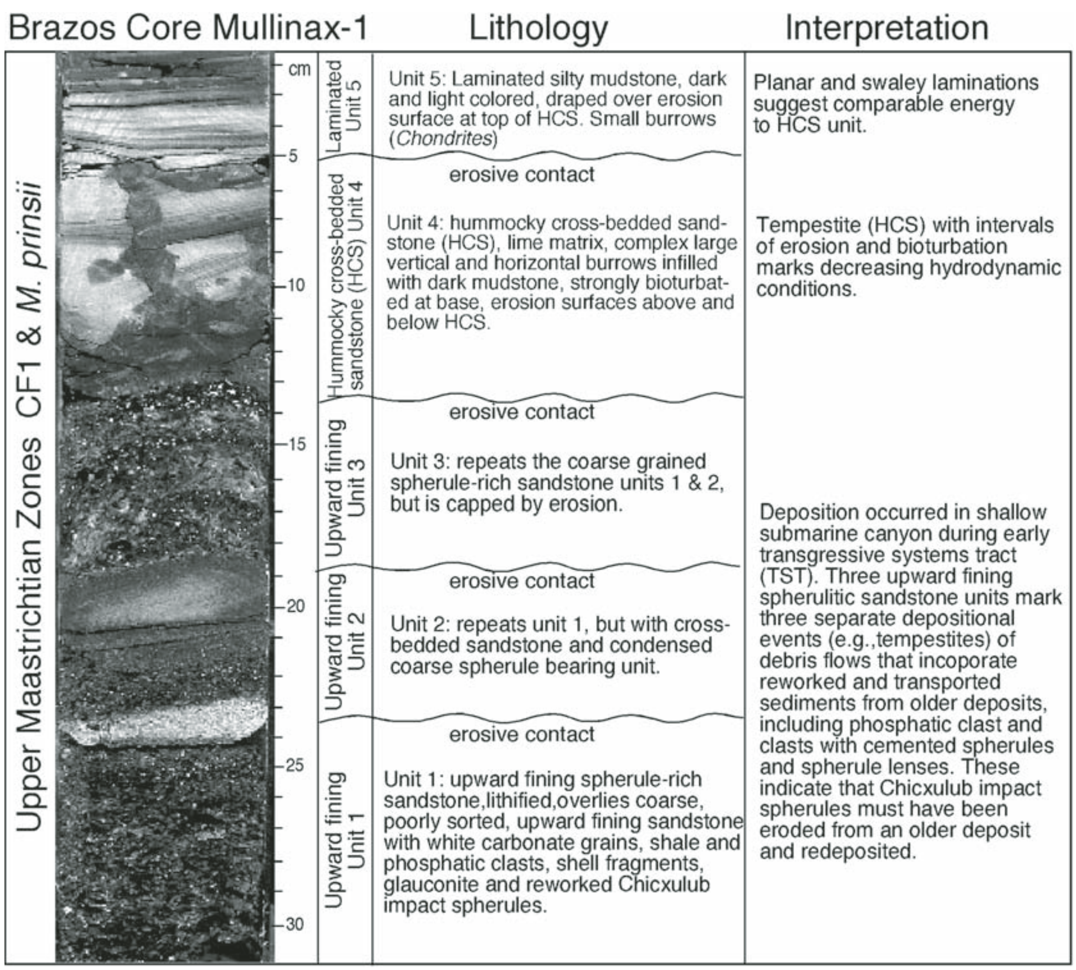


Figure 14. Sandstone complex recovered from core Mullinax-1, drilled near the Brazos River Route 413 bridge. The sandstone deposit shows three upward-fining, spherule-rich units grading into laminated fine sandstone layers. A strongly burrowed hummocky cross-bedded unit overlies the spherule-rich layers. The top of the sandstone deposit consists of a laminated clayey calcareous mudstone. This sequence is difficult to reconcile with an impact tsunami interpretation. Modified after Keller et al., 2007.

spherules, glauconite, phosphate, shell hash, and claystone clasts, which grade into finer laminated sandstones without spherules in units 1 and 2 (Fig. 14). This sequence indicates erosion, transport, and redeposition of spherules rather than the original ejecta fallout. Unit 3 is truncated by erosion and overlain by a hummocky cross-bedded sandstone (HCS) that is strongly bioturbated with large burrows infilled with dark mudstone and truncated at the top. Light and dark gray laminated silty mudstones drape over the erosion surface and contain small burrows of *Chondrites*.

This sequence indicates that deposition occurred in a shallow submarine canyon during the early transgressive systems tract (TST). The three upward-fining spherule-rich sandstone layers suggest a debris flow origin (tempestites) with erosion, transport, and redeposition of older sediments, whereas the HCS and overlying swaley and planar laminations mark decreasing hydrodynamic conditions (Keller et al., 2007).

In outcrops where the sandstone complex is well developed and overlies the scoured base of submarine canyons, a basal conglomerate bed is present of locally derived clasts from the underlying mudstone (Fig. 15A). These lithified mudstone clasts consist of hemipelagic facies and contain latest Maastrichtian planktic foraminiferal assemblages and well-preserved glass spherules (Figs. 15B and 15C). The glass spherules frequently infill fractures, or cracks, which may be rimmed by secondary sparry calcite (Fig. 15B), then truncated and followed by normal sedimentation. This suggests complex diagenetic processes and possible emergence prior to erosion and transport. These clasts with impact spherules provide unequivocal evidence of the existence of an older spherule ejecta layer, which was lithified and subsequently eroded, transported, and redeposited at the base of the sandstone deposit. In contrast, the spherules in the sandstone complex are embedded in a matrix of sand, marl clasts, glauconite, and shell fragments (Figs. 15D–15F).

Original Impact Spherule Layer

NE Mexico

Stratigraphic, lithologic, mineralogic, and paleontologic investigations of the spherule layers at the base of the sandstone complex in NE Mexico revealed these as reworked and redeposited from older sediments. In contrast to Texas, deposition occurred in an upper slope environment at a depth of at least 500 m (Keller et al., 1994a, 1994b; Alegret et al., 2001). Recently, Loma Cerca and El Peñon, which are 30 km apart, revealed the stratigraphically oldest spherule layer 8–10 m and 4–5 m, respectively, below the reworked spherule layers at the base of the sandstone complex (Figs. 1 and 12). The Loma Cerca section was discussed in Keller et al. (2002b), and only a brief summary is given here. The stratigraphically oldest spherule layer, which is between 9.5 and 10 m below the sandstone complex, is dense with spherules, some marl clasts, and foraminifera, but no sedimentary influx from shallow areas. Nearly 2 m

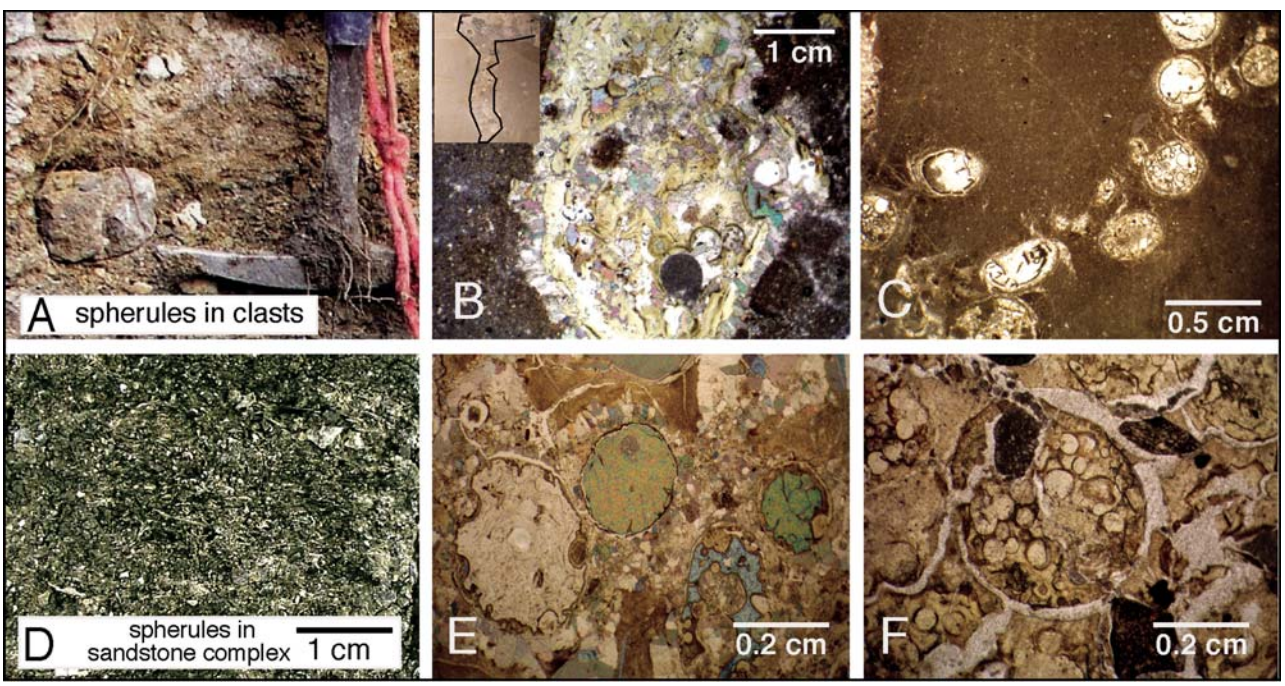


Figure 15. Spherules in mudstone clasts (A) from the basal conglomerate bed of the sandstone complex contain Chicxulub impact spherules. B and C: Some spherules infill cracks rimmed by sparry calcite and are truncated by erosion. Inset in B shows morphology of crack and total length of ~2 cm. In contrast, spherules at the base of the sandstone complex are embedded in a matrix of sand, glauconite, and shell fragments (D–F). These clasts and spherule-rich sandstones reveal the history of Chicxulub ejecta fallout, including lithification well prior to exposure to erosion, transport, and redeposition at the base of the sandstone deposit.

of marls with rare spherules and normal planktic foraminiferal assemblages overlie this spherule layer. Above it are two 50 cm thick spherule layers with upward-decreasing spherule abundance, some angular marl clasts, and anomalous peaks in robust species (e.g., globotruncanids and benthic foraminifera), which suggest reworking and redeposition.

Princeton students discovered the stratigraphically oldest spherule layer at El Peñon in upper Maastrichtian marls more than 4 m below the two spherule layers at the base of the sandstone complex (Fig. 16). Preliminary studies show an erosional base overlain by marl clasts and dense spherules cemented in calcite (10–20 cm thick; Figs. 10C and 10D) and followed by marls with decreasing spherule abundance. Four such units can be recognized in the 1.8 m thick deposit. No shallow-water fossils, wood, or plant debris, similar to the spherule deposits at the base of the sandstone complex, are present, which suggests that reworking and transport was more local. Between the top of this spherule deposit and the two reworked spherule layers at the base of the sandstone complex are ~4 m of normally bedded pelagic marls with no apparent disturbance (Fig. 16). The absence of

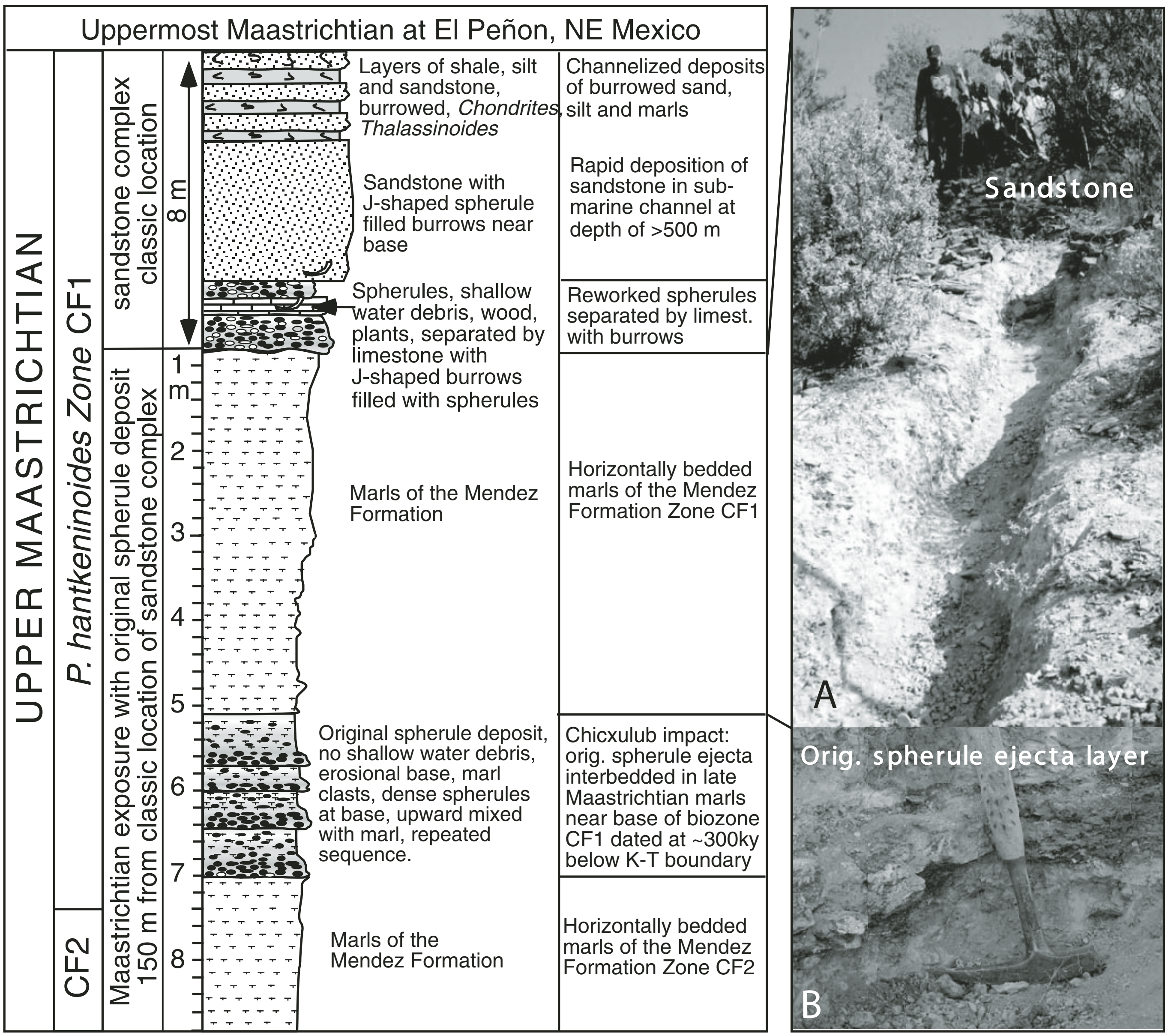


Figure 16. Composite El Peñon litholog showing the classic sandstone deposit with two reworked spherule layers at the base, and 150 m away, the newly discovered original Chicxulub impact spherule deposit near the base of zone CF1 about 4 m below the sandstone unit. A: Trenched sequence from below the sandstone unit to the original spherule deposit. Note that debris cover prevented uncovering the base of the sandstone unit. B: Base of original spherule ejecta layer.

structural disturbance of the sediments and presence of normal latest Maastrichtian microfossil assemblages indicate that these spherule layers represent the stratigraphically oldest and original Chicxulub spherule ejecta. Biostratigraphically, this spherule layer was deposited near the base of zone CF1 and thus predates the K-T boundary by ~300,000 yr.

Some workers suggested that the spherule layers in the upper Maastrichtian marls are due to large-scale earthquake-induced slumps and margin collapse (Soria et al., 2001; Smit et al., 2004) (see also *Chicxulub Debate*, http://www.geolsoc.org.uk/template.cfm?name=NSG1). However, the only evidence for structural disturbance is rare small-scale (<2 m) slumps within the upper reworked spherule layer (Keller and Stinnesbeck, 2002). In the shallow La Popa basin northwest of Monterey, Mexico, Lawton et al. (2005) described valley-like deposits as tsunami backflow, though this speculation finds little support in the sedimentary record (see Keller and Adatte, 2005; Stinnesbeck et al., 2005).

Brazos River, Texas

The original Chicxulub impact spherule layer was recently also discovered along the Cottonmouth Creek (CM) tributary of the Brazos River, Falls County, Texas, where it is best exposed below a small waterfall over the sandstone complex (Fig. 17A). At this locality, the sandstone deposit with its reworked spherules at the base is 40 cm below the K-T boundary. About 40–60 cm below the base of the sandstone deposit with its reworked spherules is a 3 cm thick yellow clay layer that consists of 100% Mg-smectite, or cheto-smectite, which is derived from weathering of glass (Fig. 17B) (Keller et al., 2007). Geochemical analysis of the smectite phases from the spherule-rich sandstone reveals the same cheto-smectite high in SiO_2 (66%–71%), Al_2O_3 (19%–20%), FeO (4.4%–4.8%), and MgO (2.8%–3.3%) with minor K_2O (1%–1.1%) and NaO (<0.5%). This composition is very similar to the altered smectite rims from glass spherules in Haiti, Belize, Guatemala, and Mexico, which indicates a common origin from altered impact glass spherules (Elliott, 1993; Debrabant et al., 1999; Stüben et al., 2002; Keller et al., 2003b). Relic glass fragments within the yellow clay and clay altered glass spherules from the base of the sandstone deposit (Fig. 15) have the same chemical composition, revealing their common origins (Keller et al., 2007, 2008). This provides very strong evidence that the yellow clay

Figure 17 (*continued on following page*). A: In Cottonmouth Creek near the waterfall, outcrops show the stratigraphic separation between the Chicxulub impact spherule ejecta layer now altered to Cheto smectite (yellow clay layer) and the sandstone complex 60 cm above. The K-T boundary is about 40 cm above the top of the sandstone complex.

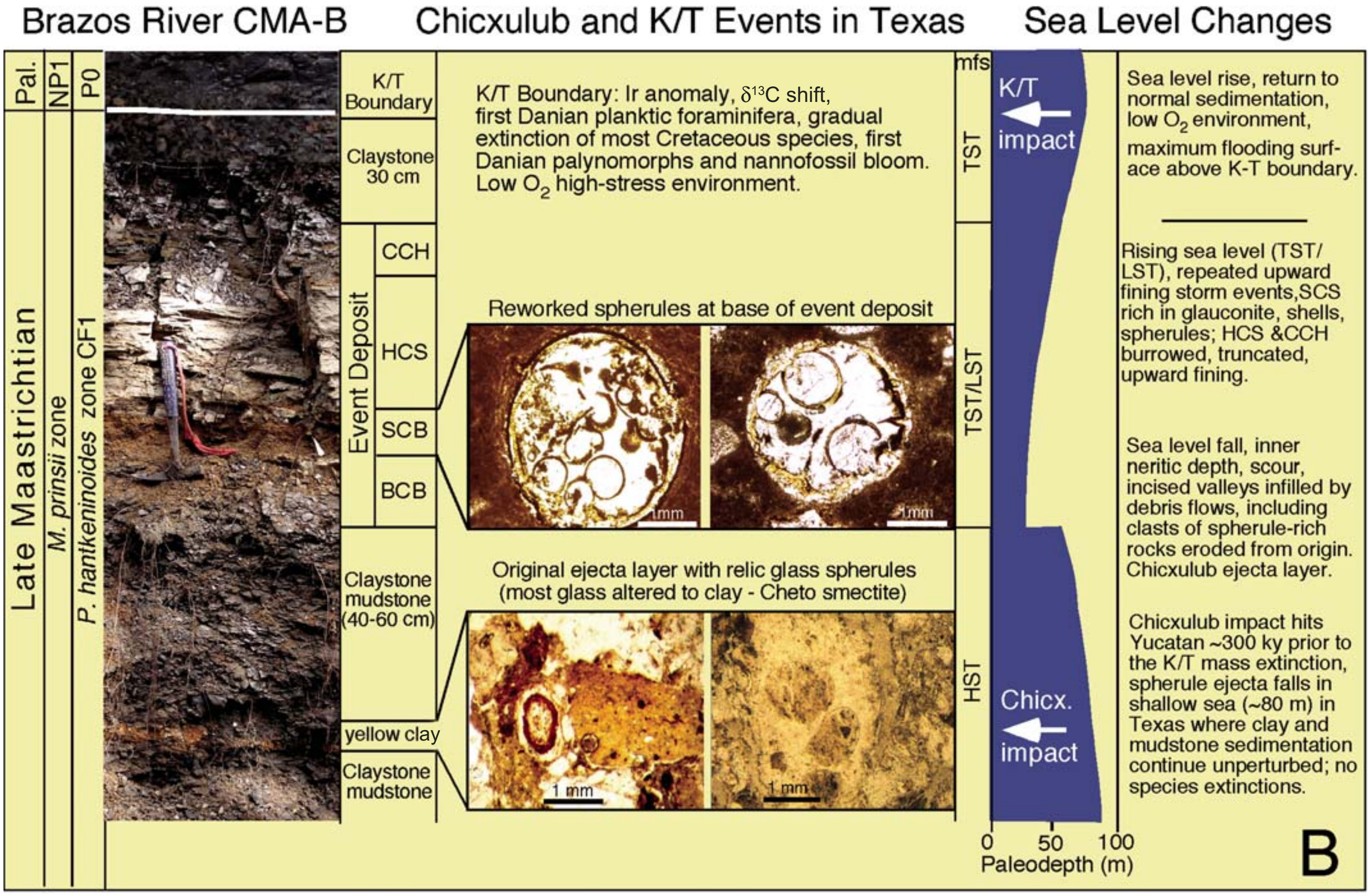


Figure 17 (*continued*). B: Cottonmouth Creek (CM) tributary of the Brazos River, Falls County, Texas. The sandstone deposit and, 40 cm below, the original Chicxulub impact spherule layer, now altered to yellow clay. The K-T boundary is 40 cm above the event deposit. The yellow clay consists of 100% Mg-smectite (cheto), indicative of altered Chicxulub impact glass; relic glass shows Chicxulub amphibolite composition. Abbreviations as in Fig 9A. Modified after Keller et al., 2007.

layer represents the original Chicxulub impact ejecta layer now altered to cheto-smectite. The stratigraphic position of this yellow clay layer near the base of zone CF1 is consistent with observations in NE Mexico and the Chicxulub crater core Yaxcopoil-1 (Keller et al., 2003a, 2004a, 2004b).

Age of Original Spherule Layer

The age of the stratigraphically oldest spherule layer can be determined from biostratigraphy. In the Brazos sections, as well as Loma Cerca and El Peñon in NE Mexico, the oldest spherule layer is near the base of planktic foraminiferal biozone CF1 (*Plummerita hantkeninoides*), which marks the last 300 k.y. of the Maastrichtian (Pardo et al., 1996). Similarly, the impact breccia in the Chicxulub crater core Yaxcopoil-1 underlies biozone CF1 (Keller et al., 2004a, 2004b). The evolutionary first appearance of *P. hantkeninoides* is thus an excellent biomarker for the age of the Chicxulub impact. This biomarker corresponds to within the lower part of nannofossil zone CC26 (*Micula prinsii*), which spans the last 450 k.y. of the Maastrichtian, and the lower part of paleomagnetic Chron 29R. The stratigraphic position and biostratigraphy thus place the Chicxulub impact in the uppermost Maastrichtian, ~300,000 yr below the K-T boundary.

This stratigraphic interval coincides with the rapid global warming that began ~450 k.y. prior to the K-T boundary and is attributed to Deccan volcanism (e.g., Kucera and Malmgren, 1998; Li and Keller, 1998b; Abramovich and Keller, 2003; Nordt et al., 2003). The climate warming follows the maximum cooling of the Maastrichtian, which culminated 500 k.y. prior to the K-T boundary and was associated with a major sea-level fall and widespread erosion. Both of these climatic events are easily identified in the stratigraphic record by paleontologic, stable isotopic, and sedimentologic analyses. Deposition of the sandstone complex coincides with the sea-level fall that followed the end of the global warming, ~100–150 k.y. before the K-T boundary. This sea-level fall resulted in widespread erosion, transport, and redeposition of the spherule layer exposed in nearshore areas.

Chicxulub Spherules in Danian Sediments

Cuba, Haiti, Belize, Guatemala, and Central Mexico

Fieldwork in Cuba, Haiti, Belize, Guatemala, and central Mexico (Fig. 1) has yielded further stratigraphic evidence that the spherule deposits in these areas are reworked and redeposited in early Danian sediments. In central Mexico (Coxquihui) a 2 cm thick altered glass spherule layer truncates the K-T unconformity, but a 60 cm thick spherule layer is in the Danian subzone P1a(1) (Fig. 7) (Stinnesbeck et al., 2002). In Bochil, Chiapas (Mexico), spherules are present in microconglomerates of the upper Maastrichtian, as well as in the early Danian subzone P1a(1) (Fig. 6). In Guatemala (Stinnesbeck et al., 1997) and Belize the K-T boundary is marked by a major unconformity with spherules and late Maastrichtian species reworked into 2–6 m of early Danian zone P1a(1) sediments, which overlie Maastrichtian platform limestone or limestone breccia (summary in Keller et al., 2003b). An Ir anomaly is present in a clayey marl in the early Danian zone P1a(1) (Fig. 18).

In Haiti, tectonic activity resulted in two K-T transitions stacked above each other, with the most commonly studied K-T boundary and spherule layers exposed in road cuts, and the less known, but more complete K-T sequences exposed on the slope ~30 m below the road (Keller et al., 2001). In these outcrops a 5–10 cm thick spherule-rich layer with early Danian zone P1a(1) planktic foraminifera and zone NP1a nannofossils directly overlies the K-T unconformity, and additional 2–4 cm thick spherule layers and spherule clasts are interspersed in the overlying 50 cm with an Ir anomaly above a rippled sandstone (Figs. 5 and 19). This spherule distribution pattern and Ir anomaly in early Danian sediments has led some workers to interpret a K-T age for the Chicxulub impact, arguing that "megaseiches" from the Chicxulub impact and subsequently seiches developed from tectonic adjustments resulted in the observed spherule redeposition (Aguado et al., 2005; Maurrasse et al., 2005). This interpretation is in conflict with the presence of early Danian species that evolved after the K-T boundary event, the apparently long-term and repeated reworking and redeposition pattern through the early Danian, and the distinct Ir anomaly in subzone P1a(1) well above the K-T boundary.

In Cuba, Alegret et al. (2005) documented the Loma Capiro section near Santa Clara. In the same area, Stinnesbeck, Adatte, and Keller analyzed the Santa Clara section where exposure of the breccia is limited to the top 10 m (Fig. 20). The two sequences are complementary, but there are some differences in the breccia and overlying Danian. In the Loma Capiro section,

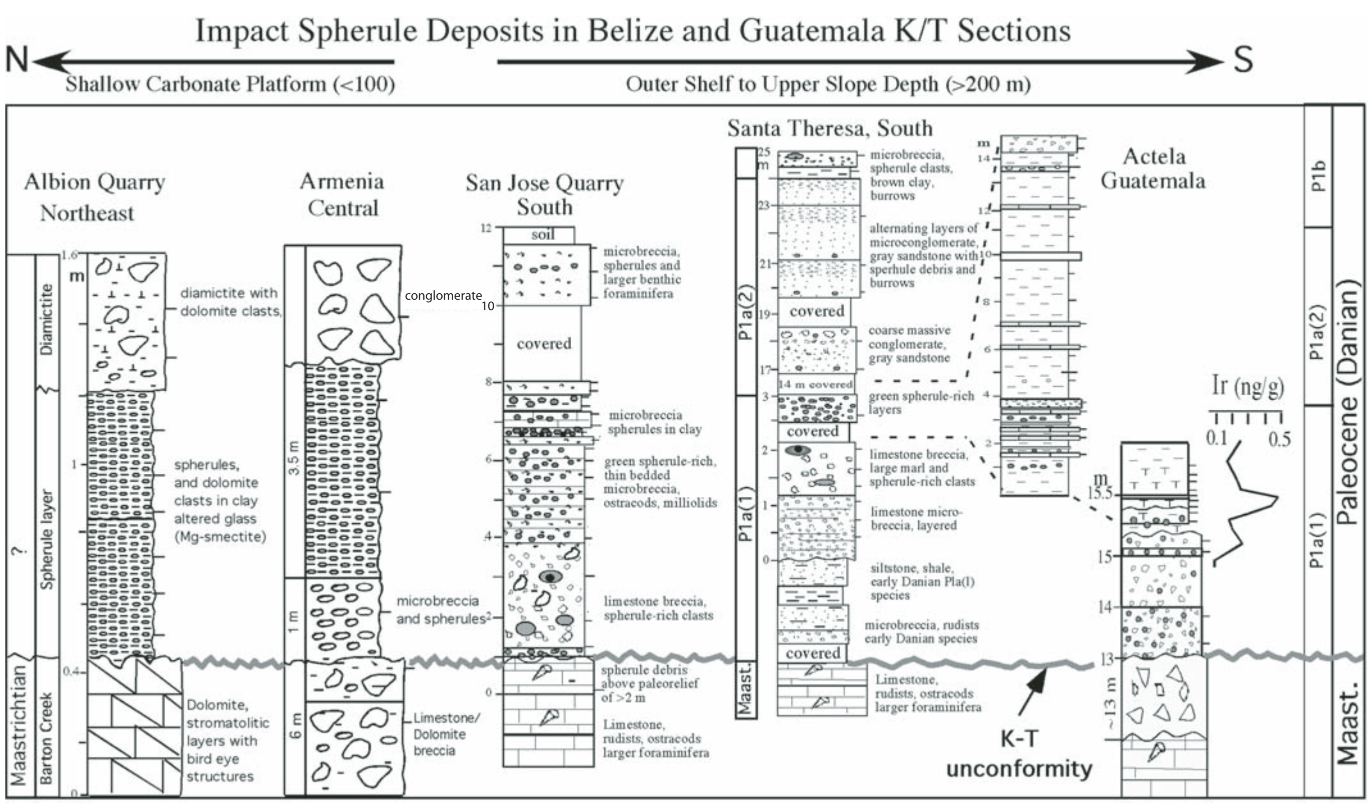


Figure 18. Litho- and biostratigraphy of the Belize and Guatemala K-T sequences from shallow platform environments in the north to deeper outer shelf and upper slope sequences in the south and Guatemala to the west (modified after Keller et al., 2003b). A major unconformity marks the K-T boundary, and all spherule deposits are reworked into early Danian sediments. An Ir anomaly is present in zone P1a(1) in the Actela section of Guatemala.

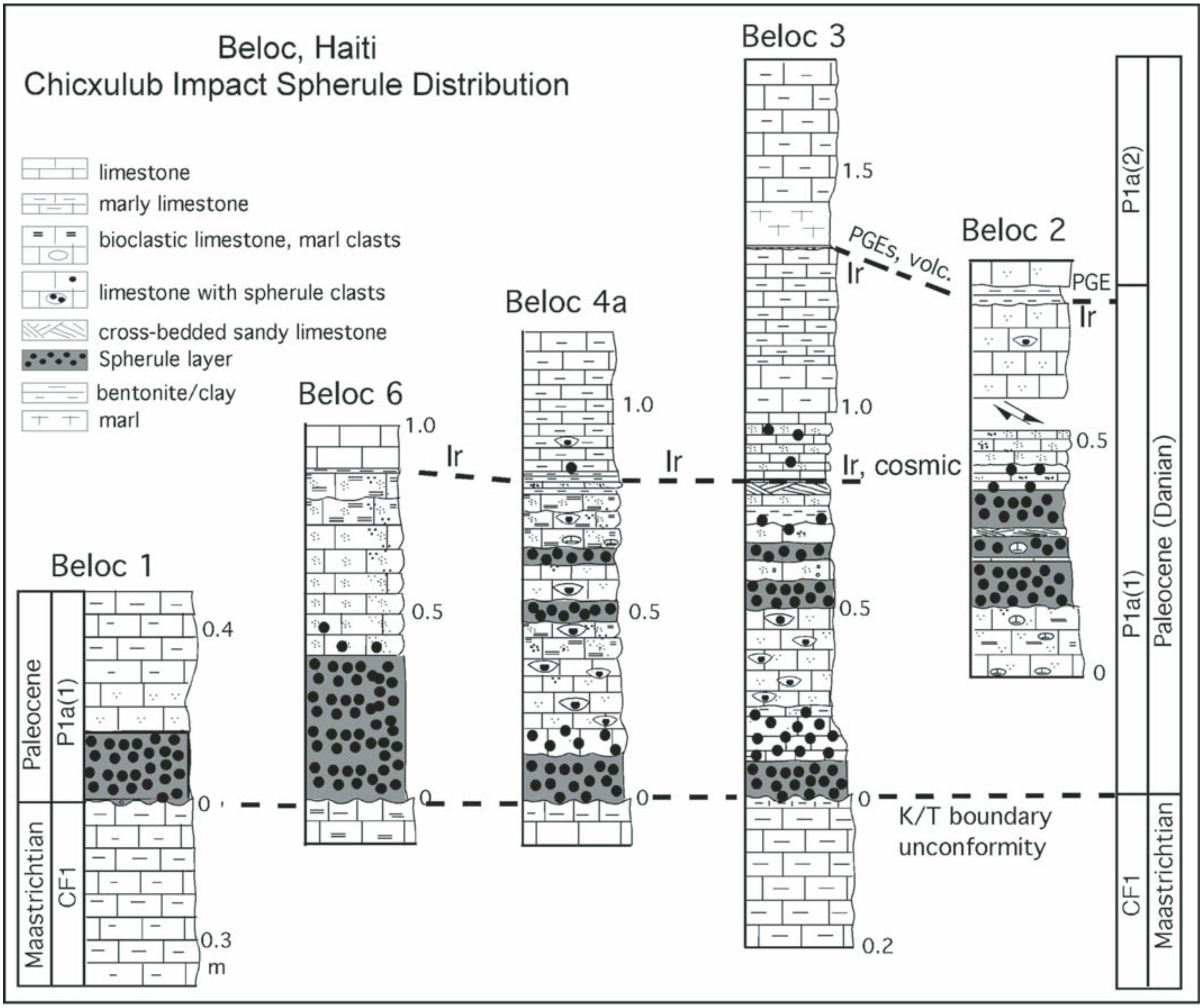


Figure 19. Litho- and biostratigraphy of the Beloc, Haiti, K-T sequences (modified after Keller et al., 2001). All spherule-rich deposits are reworked into early Danian zone P1a(1), as indicated by the presence of early Danian index species and reworked Cretaceous species. An Ir anomaly of cosmic origin is present above the spherule-rich sediments and a Pd anomaly of volcanic origin is present at the P1a(1)-P1a(2) boundary.

the breccia consists of an upward-fining megabreccia, followed by an upward-fining microconglomerate and topped by upward-fining sandstone with spherules at the top. In the Santa Clara section, the upward-fining microconglomerate and sandstone are absent. An undulating erosion surface with the depressions filled by altered glass spherules marks the top of the megabreccia. About 5 cm above this unconformity is a 1 cm thick spherule layer in marlstone. The overlying Danian sequence appears to be the same in both sections, consisting of clayey siltstone or marlstone with sand layers. Alegret et al. (2005) recognized upper zone P1a (or Pα) assemblages above the unconformity and estimated that a hiatus spans zone P0 and most of P1a. At Santa Clara, the presence of rare small *P. eugubina* in an assemblage of *Subbotina triloculinoides* and *Parasubbotina pseudobulloides* marks this interval as the upper part of zone P1a, or P1a(2), in agreement with Alegret et al. (2005).

The breccia contains reworked Maastrichtian species, including the zone CF1 index *Plummerita hantkeninoides*. Alegret et al. (2005) argued that the presence of this species in the breccia excludes a pre-K-T age for the Chicxulub impact. However, this is not the case because in NE Mexico and Texas the original Chicxulub impact ejecta layer is *near the base of zone CF1*—indicating that the impact occurred after the first appearance of *P. hantkeninoides*. This suggests that breccia formation is

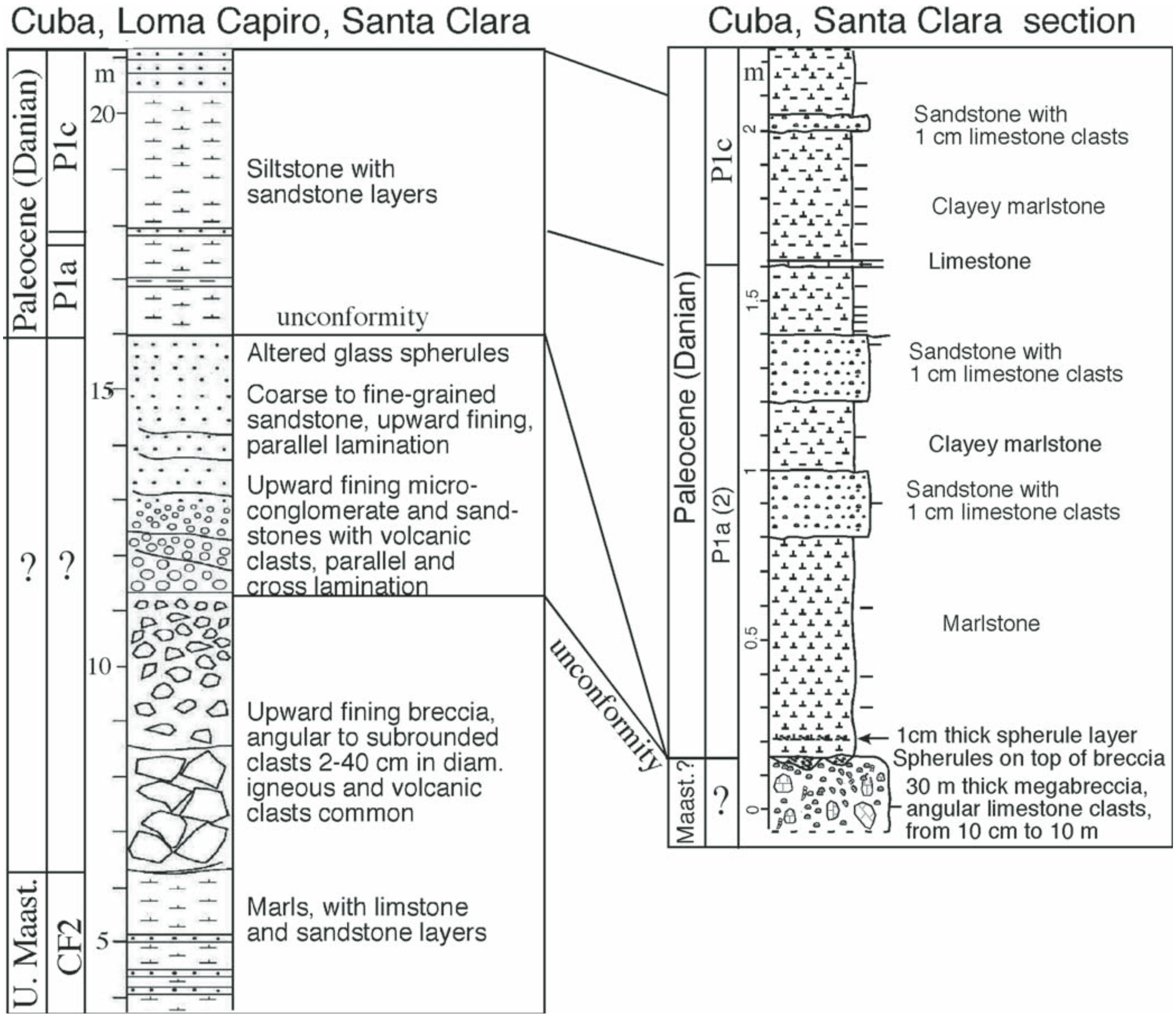


Figure 20. Litho- and biostratigraphy of the Cuba K-T sequences near Santa Clara. The Loma Capiro section (modified after Alegret et al., 2005) has a more expanded breccia complex than the Santa Clara section. In both sections, Chicxulub spherules are present at or above the unconformity between the breccia complex and the overlying Danian sediments. The early Danian zones P0 and P1a(1) are missing at the unconformity.

no older or younger than the base of zone CF1, similar to the age of the impact breccia in Yaxcopoil-1 (Keller et al., 2004a, 2004b). The stratigraphic position of the spherules at the top of the sandstone unit in Loma Capiro and in the Danian zone P1a above the unconformity in the Santa Clara section indicates reworking and redeposition and does not support a K-T age for the Chicxulub impact, as suggested by Alegret et al. (2005).

The Cuba and Haiti spherule distribution patterns are similar to those observed in Belize and Guatemala and represent post-depositional erosion and redeposition during the early Danian. These Central American sequences illustrate the danger of basing interpretations on regional observations that may reflect special marine settings (e.g., shallow platform limestones) or tectonic activities that resulted in incomplete sequences. These sections must be interpreted within the context of the more complete and high-sedimentation deepwater sequences of NE Mexico and the shallow-water sequences in Texas.

Chicxulub Spherules and Ir Anomaly in Stratigraphic Proximity

Advocates for a K-T age of the Chicxulub impact frequently point to the stratigraphic proximity of spherules and an Ir anomaly in terrestrial sequences of the continental United States and some deep-sea marine sequences (e.g., Blake Nose, Bass River, Demerara Rise) as unequivocal evidence that Chicxulub caused the K-T mass extinction (Olsson et al., 1997; Norris et al., 1999, 2000; Klaus et al., 2000; MacLeod et al., 2006). Differential settling of iridium and spherules, estimated at a few hours to days, is often used to explain the proximity of the Ir anomaly at or a few centimeters above the spherule layer in the deep-sea and terrestrial sequences. This argument is plausible only if there is no inverse grading in the spherule layer and no disconformity due to erosion and/or nondeposition—features that are evident at Blake Nose, Bass River, and Demerara Rise.

Stratigraphic proximity of the Ir anomaly and spherule layer alone is no proof for a cause-and-effect relationship, particularly in the deep-sea and terrestrial records, where sedimentary sequences tend to be incomplete due to erosion or condensed sedimentation. Deep-sea marine sequences must be interpreted with caution, as they contain almost invariably less complete sedimentation records than continental shelf sequences. This is because the sedimentation rate is higher on shelves due to terrigenous influx, whereas erosion is higher in the deep sea due to intensified current circulation during climate cooling and lower sea levels, such as during deposition of the latest Maastrichtian zone CF1 sandstone deposits.

Blake Nose, Western North Atlantic

Perhaps the most commonly cited example for a cause-and-effect relationship between impact and Ir anomaly is Blake Nose ODP Site 1049 (Sigurdsson et al., 1997; Norris et al., 1999, 2000; Klaus et al., 2000; Martínez-Ruiz et al., 2002). At this locality, a 15 cm thick spherule layer disconformably overlies slumped carbonate ooze of upper Maastrichtian age (Fig. 21). The spherule layer is graded and contains clasts of limestone, dolomite, chert,

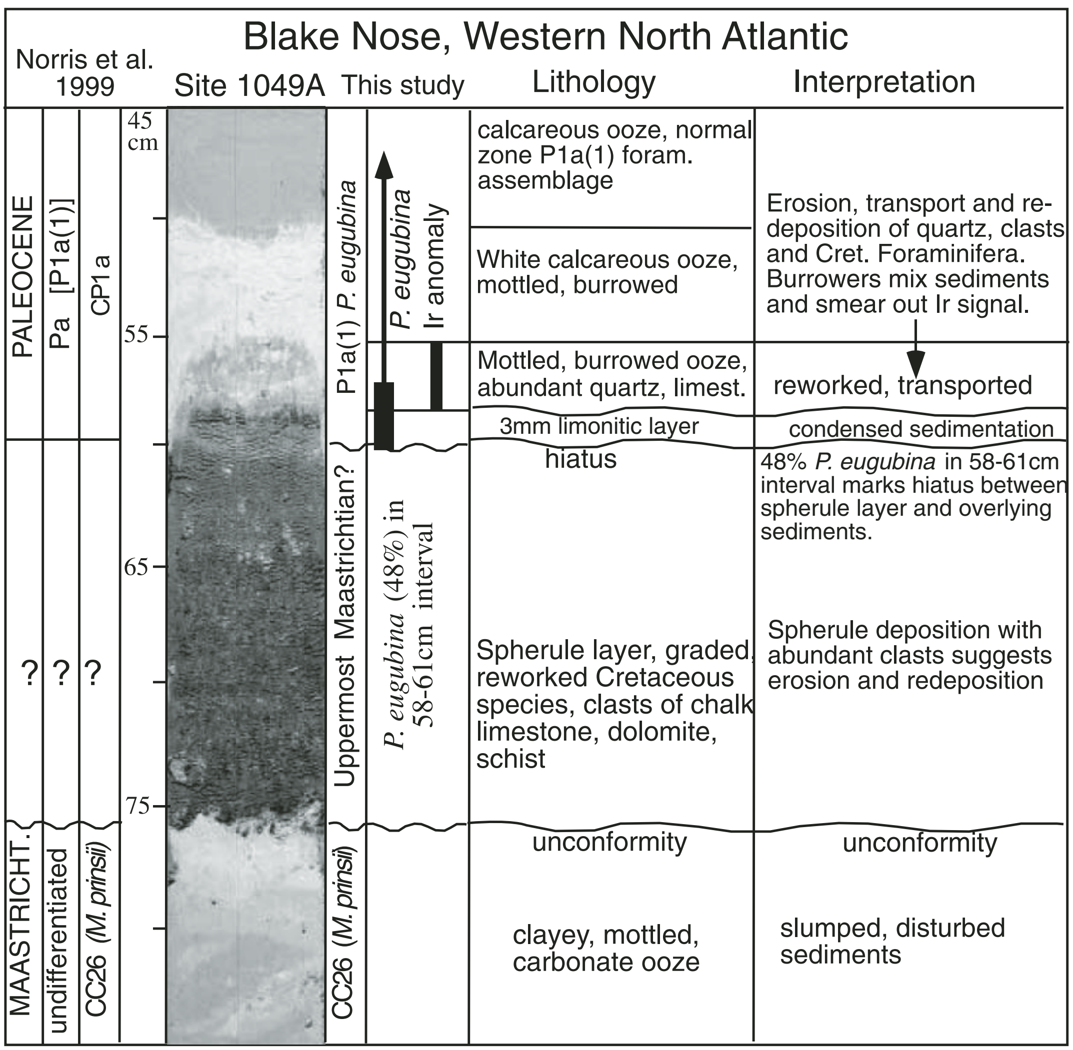


Figure 21. Litho- and biostratigraphy of ODP Site 1049A, Blake Nose, western North Atlantic (modified after Norris et al., 1999). Note that this section contains a highly condensed K-T transition that is disturbed, burrowed, mixed, and incomplete. The juxtaposition of the spherule layer and Ir anomaly in this sequence permits no conclusion as to the precise timing of the Chicxulub impact.

and schist, which indicate reworked and transported sediments. Above it is a 3 mm thick limonitic layer followed by a 3–4 cm thick dark gray mottled and bioturbated ooze that contains abundant quartz, limestone chips, Cretaceous foraminifera, 48% of the Danian species *Parvularugoglobigerina eugubina*, and an Ir anomaly (1.3 ppb). The presence of quartz, limestone chips, and Cretaceous foraminifera indicate that this layer is also reworked. Norris et al. (1999) concluded that the basal Danian zone P0 (e.g., boundary clay) is absent. Nevertheless, they interpreted this mottled and disturbed interval as a complete sedimentary sequence and unequivocal evidence that the Chicxulub impact is the K-T boundary event.

To justify this conclusion, they explained the absence of the boundary clay zone P0 by arguing that it does not exist in the deep sea (Norris et al., 1999). They based this conclusion on their analysis of the K-T clay at the El Kef stratotype section, stating that they found rare tiny *P. eugubina* at the base of the clay layer where no others had detected them. However, the specimen they show is large (80 µm, whereas the first specimens are usually <63 µm; Keller et al., 1995, 2002a), well developed, and known to occur much later in its evolutionary history, which suggests contamination or mixing probably by bioturbation. Without further evidence, Norris et al. (1999) speculate that zone P0 may be an artifact of rare occurrence of *P. eugubina* in shallow-water sequences, whereas in deep waters this species would be more common. They conclude that if P0 is interpreted as a shallow-water biofacies—and hence absent in the deep—then "*the deep-sea sites are biostratigraphically complete and can be used to describe events immediately surrounding the impact event*" (Norris et al., 1999, p. 421). This argument does not take into account that El Kef, deposited in 300–500 m depth, is not a shallow-water sequence, and that the K-T boundary clay, or zone P0, has been documented in deep-sea sequences worldwide beginning with the Gubbio section in 1980 and in NE Mexico localities in the 1990s.

The stratigraphic and sedimentary record of Site 1049A provides evidence for a simpler interpretation (Fig. 21). The close stratigraphic proximity of the spherule layer and Ir anomaly is marked by discontinuity, nondeposition, erosion, and redeposition. For example, after spherule deposition the 3 mm limonitic layer marks a period of condensed sedimentation or nondeposition. Above it, the 3–5 cm burrowed mottled dark and light ooze indicates slow deposition with abundant burrowing organisms during a time of erosion, transport, and redeposition. The high abundance (48%) of *P. eugubina* in the 58–61 cm interval overlying the spherule layer (this study) marks a hiatus with the early part of zone P1a(1) missing. In condensed, burrowed, mixed, and incomplete sequences, it cannot be determined whether the Ir anomaly and well-developed *P. eugubina* represent the K-T or second Danian P1a(1) Ir anomaly of the region (discussed above). The main point here is that the juxtaposition of the spherule layer and Ir anomaly in Site 1049 provides no proof of cause and effect, but appears to be an artifact of a condensed and incomplete stratigraphic record that permits no conclusion as to the precise timing of the Chicxulub and K-T events.

Demerara Rise, Western North Atlantic

ODP Leg 207, Site 1259, on Demerara Rise recovered a K-T transition similar to Site 1049 on Blake Nose. The K-T transition was recovered in four closely spaced holes, each with an ~2 cm thick spherule layer separating Cretaceous chalk from overlying Paleogene claystone. MacLeod et al. (2006) described the lithology of Hole 1259B, but provide Ir and biostratigraphic data from 1259C, where an Ir anomaly of 1.5 ppb coincides with the very top of the spherule layer and high values (0.5–0.7 ppb) persist over 15 cm of the claystone (Fig. 22), which suggests mixing of the original signal. They report very low-diversity (five to ten species) late Maastrichtian zone CF1 assemblages, indicating high-stress conditions. A similar assemblage is present in the spherule layer. A thin section of the basal clay above the spherule layer shows an assemblage dominated by *Guembelitria cretacea*, which is characteristic of high-stress conditions after the mass extinctions, as well as shallow water or restricted basin environments of the latest Maastrichtian (Keller, 2002; Keller and Pardo, 2004). Therefore, this interval can only be questionably assigned to P0 on the basis of abundant *Guembelitria*. The first Danian species are reported 6 cm above the spherule layer and mark the *Parvularugoglobigerina eugubina* P1a(1) zone (MacLeod et al., 2006), though the presence of *Chiloguembelitria crinita* indicates that this is not the basal part of this zone. Thus, the position of the spherule layer stratigraphically separates Cretaceous and Paleogene sediments, but the continuity of sedimentation and the history of spherule and Ir deposition are in doubt.

MacLeod et al. (2006, p. 10) argue that the K-T boundary should be placed at the base of the spherule layer, because this is in agreement with the impact signals (e.g., spherules, shocked quartz, Ir anomaly) at the El Kef stratotype and shows that the Chicxulub impact defines the K-T boundary. They interpret the juxtaposition of the Ir anomaly and spherule layer as unequivocal evidence that the Chicxulub impact defines the K-T boundary (p. 12) and demonstrates "*first-order agreement with the predictions of the impact hypothesis*" recording the history "*within minutes of the impact.*" There are major problems with this interpretation.

For example, there are no Chicxulub-type spherules at the El Kef stratotype, and no Ir anomaly has ever been recorded in association with the Chicxulub spherule layers. The juxtaposition of spherules and Ir anomaly has only been reported from the condensed and apparently incomplete deep-sea sections on Blake Nose, Bass River, and Demerara Rise. In areas of high sedimentation rates and thick (~2 m) spherule layers (e.g., NE Mexico and Brazos River, Texas), the K-T Ir anomaly and Chicxulub spherule layers are well separated by 2–9 m of undisturbed marls or claystones (Figs. 14, 16, 17). This suggests that the juxtaposition of the two impact signals on Demerara Rise is an artifact of a condensed and incomplete sedimentary record. Another potential problem is the inverse grading and soft-sediment deformation (e.g., fine-grained white layers at the base of the spherule layer followed by upward-fining spherules; Fig. 22), which MacLeod et al. (2006) interpreted as dewatering and resuspension of fines

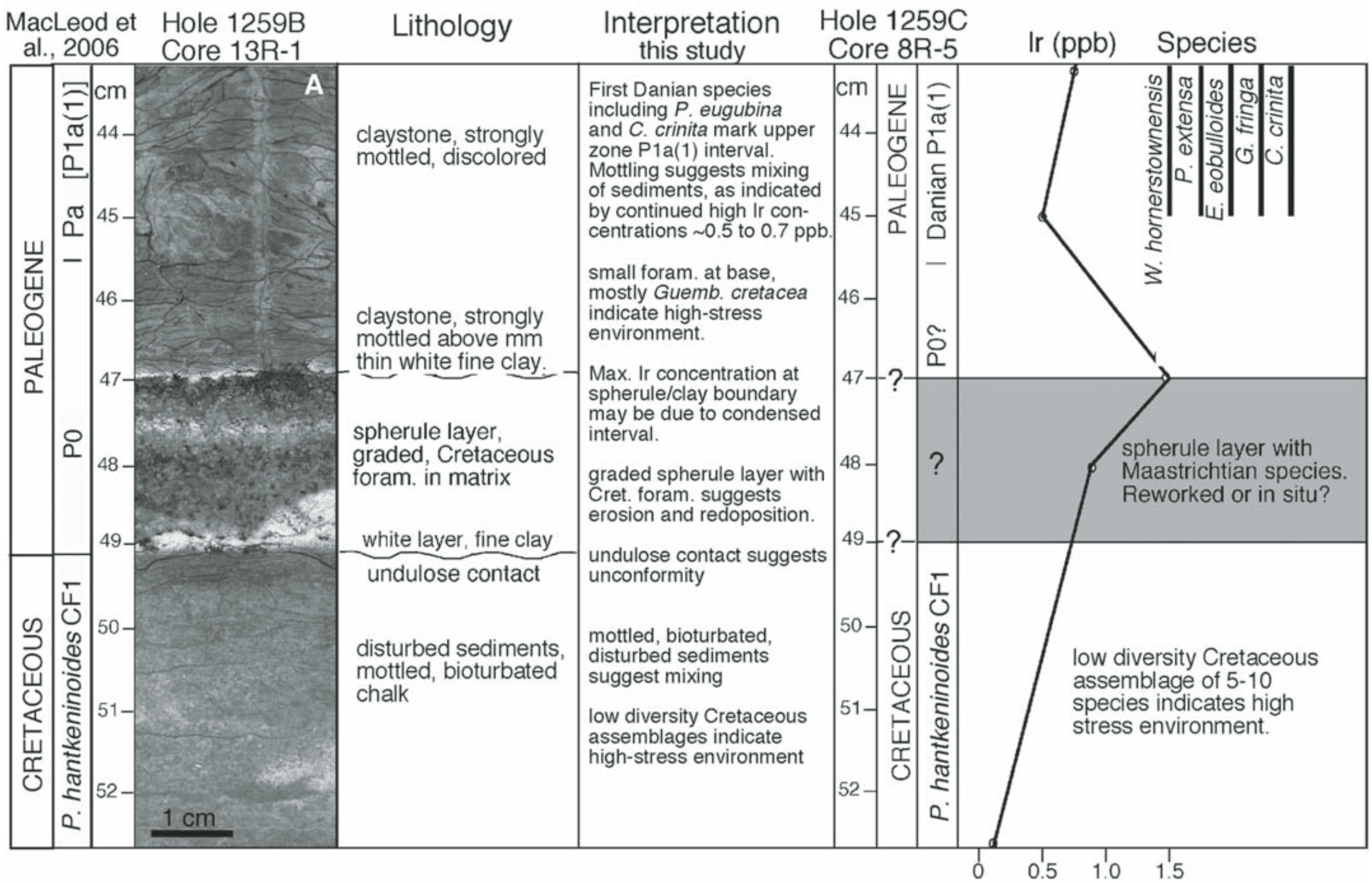


Figure 22. Litho- and biostratigraphy of ODP Site 1259, Demerara Rise, western North Atlantic (modified after MacLeod et al., 2006). Note that this section is very similar to Blake Nose Site 1049, though has the latest Maastrichtian zone CF1 present. Although the spherule layer and maximum Ir concentrations followed by the first Danian species place this impact ejecta at or near the K-T boundary, lithological characteristics indicate condensed sedimentation and redeposition (inverse grading), which allows no conclusion as to the timing of the Chicxulub impact.

as a result of seismic shaking within 15 min of the impact. An alternative explanation is reworking and resettling of sediments during intensified current circulation associated with the end-Maastrichtian global cooling and low sea level that resulted in erosion and redeposition of spherules throughout Central America, the Caribbean, and Texas (Keller et al., 2003a, 2007).

Bass River Core, New Jersey

The Bass River core of New Jersey has also been claimed to contain a complete K-T boundary sequence that provides "unequivocal evidence" that the Chicxulub impact is K-T in age (Olsson et al., 1997). However, this shallow-water (~100 m) sequence is demonstrably incomplete. The Maastrichtian consists of highly bioturbated glauconitic clay with only the top 8 cm indicative of the *M. prinsii* (CC26) zone, which suggests erosion of the uppermost Maastrichtian sediments (Fig. 23). The overlying spherule layer is poorly sorted with altered clay spherules and clasts. Above it is a silty glauconitic clay with numerous clasts with Maastrichtian microfossils that indicate erosion, transport, and redeposition. The presence of an early Danian planktic foraminiferal assemblage with six species, including *P. eugubina*, marks zone P1a as spanning a mere 8 cm interval. This indicates that the boundary clay zone P0 and most of zone P1a are missing in the Bass River core. The juxtaposition of the spherule layer and early Danian is due to a major hiatus, which allows no conclusion as to the timing of the Chicxulub event.

Terrestrial Sequences—U.S. Western Interior

Another frequently used argument in support of Chicxulub as the K-T boundary impact is the close proximity of the spherule and Ir-enriched layers in terrestrial sequences from the U.S. Western Interior (Orth et al., 1982). In these localities a 2 cm thick gray layer of kaolinite and some smectite and hollow goyazite spherules (infilled by kaolinite) mark the Chicxulub spherule layer. Above it is a dark organic-rich thinner layer of laminated smectite and kaolinite clay with shocked minerals and siderophile elements that is believed to mark the K-T boundary "fireball" layer (Bohor, 1990; Izett, 1990; Bohor and Glass, 1995). However, sedimentation in terrestrial sequences is inherently discontinuous, and the close stratigraphic proximity

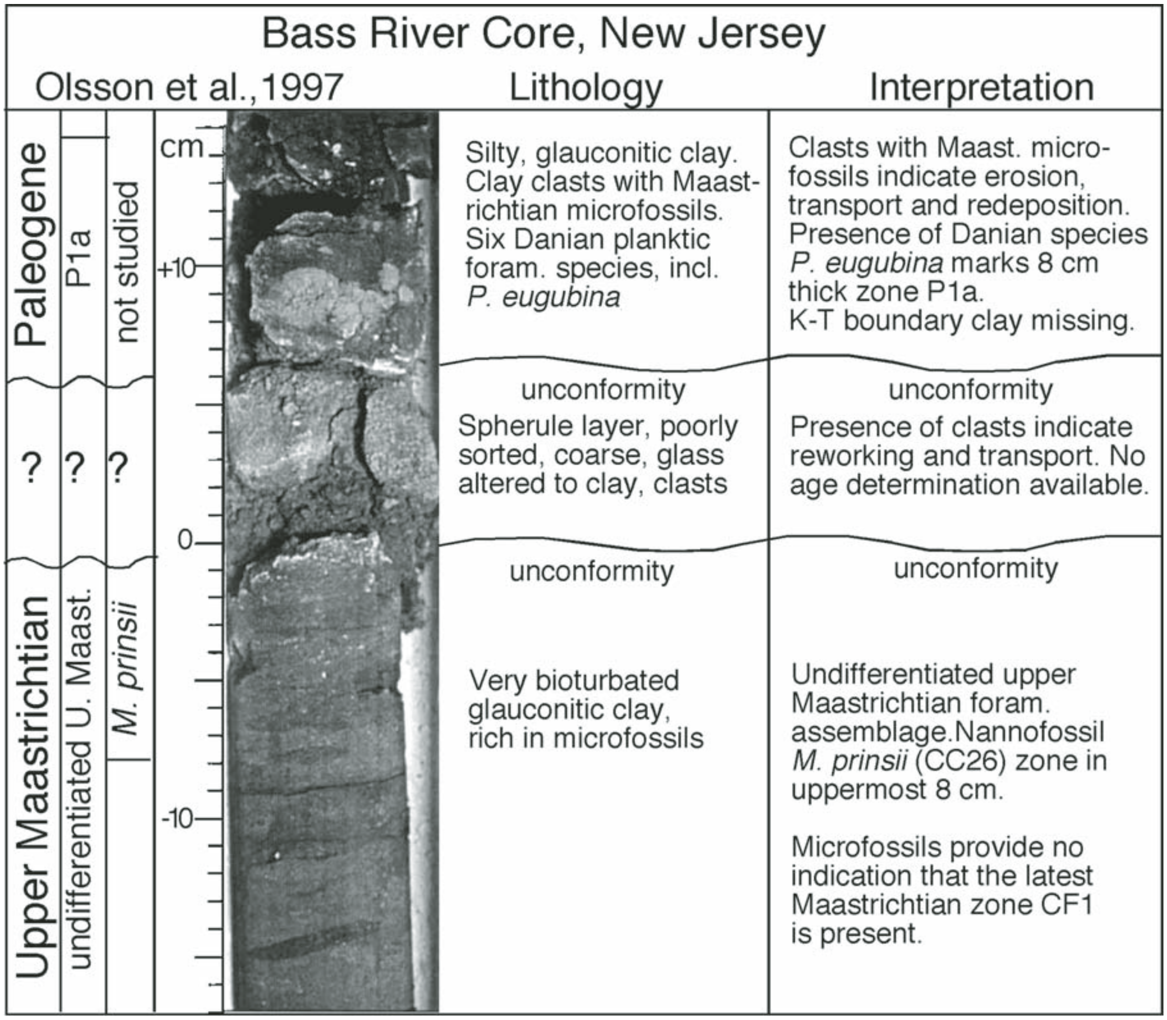


Figure 23. Litho- and biostratigraphy of the Bass River core of New Jersey (modified after Olsson et al., 1997). In this section the juxtaposition of the spherule-rich layer and the overlying 8-cm-thick glauconitic clay of zone P1a marks a major hiatus, which allows no conclusion as to the timing of the Chicxulub event.

of two separate layers alone is not a convincing argument for a cause-and-effect scenario.

DISCUSSION AND SUMMARY

The promise and potential of impact stratigraphy are impact markers as time horizons in correlation and in deciphering the relative order of a closely spaced sequence of events. In principle, impact markers represent an instant in time, and their stratigraphic positions relative to other marker horizons are fixed, providing a time line between younger and older events above and below. But impact markers are subject to the same geological forces as any other marker horizons—erosion, reworking, and redeposition—sometimes leaving multiple impact marker horizons over time from which the postdepositional history must be carefully evaluated.

The global K-T Ir anomaly and more regional Chicxulub impact spherules are the most widespread and consistently present impact markers, and both have been used as unquestionable K-T marker horizons. However, strata with Ir anomalies never contain Chicxulub impact spherules and spherule layers never contain iridium anomalies. Moreover, the stratigraphic position of the oldest spherule layer is in undisturbed upper Maastrichtian sediments. But reworked and redeposited spherule layers are common in the uppermost Maastrichtian and lower Danian, and there is evidence of additional Ir anomalies of both cosmic and volcanic origins in the early Danian (Fig. 24). In the deep sea, the sedimentary records are generally condensed and incomplete due to erosion and nondeposition, which may position the Ir anomaly in close proximity with a thin (1–2 cm) spherule layer. For these reasons, analysis of isolated sequences can lead and has led frequently to erroneous conclusions.

A comprehensive survey of Ir anomaly and spherule impact markers within the Chicxulub proximal and distal ejecta fields from Texas to central Mexico and the Caribbean reveals the main

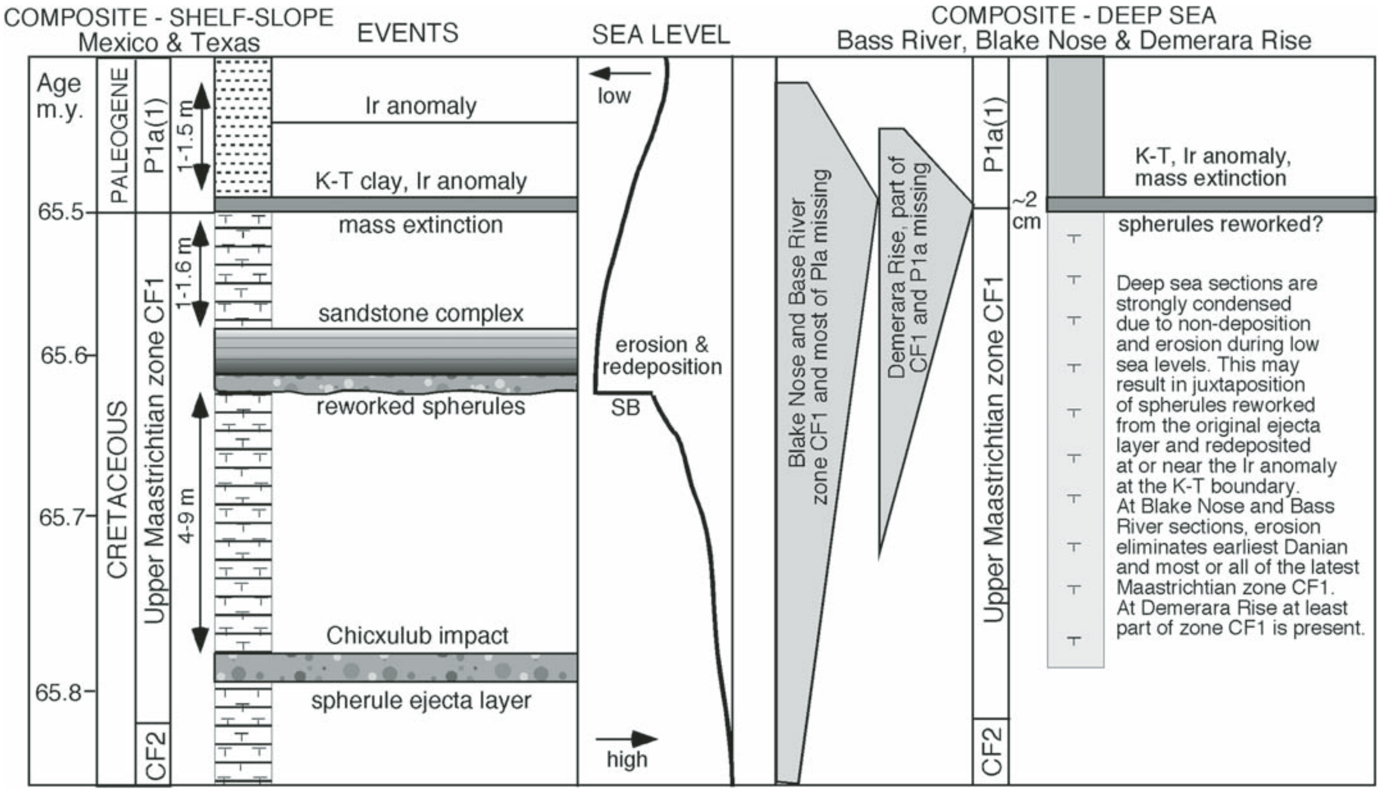


Figure 24. Summary of impact horizons in upper Maastrichtian to lower Danian sediments based on the composite stratigraphy of the most expanded shelf and upper slope sequences in Texas and NE Mexico. The original Chicxulub impact ejecta spherule layer, the reworked spherules at the base of the sandstone complex, and the K-T Ir anomaly are all excellent marker horizons. Comparison with the condensed marine sequences in the northeastern Atlantic indicates that these three marker horizons are condensed into one, juxtaposing the Ir anomaly and spherules at or near the K-T boundary due to erosion and nondeposition.

Ir anomaly at the K-T boundary clay (red layer), consistent with its global occurrence, and a second smaller Ir anomaly of cosmic origin and one of volcanic origin in the early Danian zone P1a(1) (Stüben et al., 2002, 2005). The K-T transition is thus marked by multiple impacts, similar to the late Eocene, the end-Devonian, and the Triassic (Keller, 2005).

The stratigraphy of impact spherules is even more complex than that of Ir anomalies, due to erosion, transport, and redeposition of spherules, and varies on a regional basis, apparently controlled by gravity flows and slumps commonly associated with sea-level falls. For example, impact spherules from predominantly shallow-water sequences of southern Mexico, Guatemala, Belize, Haiti, and Cuba are reworked and redeposited in the early Danian zone P1a(1). An unconformity marks the K-T boundary, and in some localities rare spherules can be found in the underlying breccia (e.g., Chiapas and Guatemala). In NE Mexico and Texas, impact spherules are exclusively found in upper Maastrichtian sediments, with the stratigraphically lowermost and original impact ejecta layer near the base of zone CF1, ~300,000 yr below the K-T boundary.

It is tempting to interpret this pattern of spherule layers as evidence for multiple impacts. But this is not supported by spherule glass geochemistry, which indicates comparable compositions in all spherule layers and is consistent with impact glass in the Chicxulub crater cores (e.g., Schulte et al., 2003; Keller et al., 2007). This indicates that all stratigraphically higher spherule layers are reworked from the stratigraphically oldest and original ejecta deposit. In all areas with abundant spherule deposits, redeposition of impact spherules occurred predominantly in submarine canyons during the latest Maastrichtian sea-level fall (~100–150 k.y. prior to the K-T boundary; Fig. 24), which also deposited a widespread sandstone complex that has been erroneously interpreted as a megatsunami generated by the Chicxulub impact.

Although impacts create tsunamis, which are expected to leave sedimentary records, there is little disturbance associated with the original impact ejecta layer at Brazos River in Texas, and Loma Cerca and El Peñon in NE Mexico, at 500 km and 1000 km, respectively, from the impact crater on Yucatan. The submarine canyon sandstone deposits with reworked spherules at the base were formed much later (probably ~100–150 k.y. prior to the K-T boundary) during a sea-level fall that lowered sea level by ~50–70 m, as estimated from Brazos River sequences. Clasts with spherules from the original deposit and burrowed horizons throughout these sandstone complexes indicate long-term deposition and seasonal storms rather than a tsunami (Yancey 1996; Gale, 2006).

Impact stratigraphy is thus an exceedingly useful tool in stratigraphy that can help evaluate the sequence of events across critical intervals in Earth's history. But it has to be used with caution, applied on a regional scale to avoid isolated artifacts of redeposition, and subject to the basic stratigraphic principle of superposition—that *in any undisturbed sediment sequence the oldest bed is at the base and the youngest at the top*. Observations from this regional evaluation of Ir and spherule impact markers provide some guidance.

Iridium Marker in K-T Sequences

The sharp K-T iridium anomaly is probably the best impact marker, though studies in India suggest that a volcanic origin cannot be excluded (Bajpai and Prasad, 2000). Because of its properties, Ir is unlikely to be reworked and redeposited as a sharp peak anomaly (Sawlowicz, 1993), though it is easily smeared out by bioturbation. In NE Mexico, as in continuous sequences worldwide, the K-T Ir anomaly is only found in the boundary clay or thin red layer, coincident with critical K-T markers such as the negative $\delta^{13}C$ shift, the extinction of all specialized tropical planktic foraminifera, and evolution of the first Danian species in the boundary clay immediately above (Fig. 4). When used together with these bio- and chemomarkers, the Ir anomaly is a reliable K-T indicator. However, it requires some considerations.

1. In NE Mexico the Ir anomaly is in the K-T boundary clay and red layer and stratigraphically always above the sandstone complex with its spherules at the base (e.g., El Mimbral, La Parida, La Sierrita; Figs. 8A and 8B). Along the Brazos River, Texas, the Ir anomaly is also above the sandstone complex with spherules at the base (Figs. 9A and 9B).
2. Ir can be remobilized upward and downward and concentrated at redox boundaries, though in usually much smaller concentrations. Such minor Ir enrichments are present in the sandstone complex below the K-T boundary at El Mimbral and Brazos-1 (Figs. 8A, 8B, 9A, 9B) and have been claimed as support for the impact tsunami hypothesis and to justify the placement of the K-T boundary at the base of these sandstone complexes. Ir anomalies cannot be used in isolation as the sole index for the stratigraphic placement of the K-T boundary.
3. Iridium anomalies are not unique and therefore not infallible K-T markers. At least three impact craters are known during the last several hundred thousand years of the Maastrichtian (Silverpit, Boltysh, Chicxulub). The fourth may be the K-T impact for which no impact crater is yet known. A fifth impact may have occurred during the early Danian zone P1a(1). Ir anomalies are known only from the K-T and Danian impacts.
4. Iridium anomalies may be of cosmic or volcanic origins. In particular, small Ir anomalies should be used with caution and require other PGEs to determine their origin (e.g., cosmic, volcanic, or redox boundaries). For example, early Danian zone P1a(1) sediments in Haiti, Guatemala, and central Mexico contain an Ir anomaly of cosmic origin, but in Haiti a second small Ir anomaly is of volcanic origin (Fig. 5).
5. No iridium enrichment has been observed to date in any impact spherule layers or any other Chicxulub impact ejecta. The Chicxulub bolide may have been a dirty snowball–type comet without Ir enrichment.

Chicxulub Spherule Marker in K-T Sequences

The geographic and stratigraphic distribution of the Chicxulub impact spherules is very complex due to the postdepositional history affecting these deposits (e.g., tectonic, erosion, transport, redeposition, slumps, gravity flows). The multiple stratigraphic occurrences of altered glass spherules show how easily spherules can be transported and redeposited into younger sediments. Their presence in both uppermost Maastrichtian and lower Danian sediments reflects repeated erosion and redeposition of spherules over several hundred thousand years after the impact event. This limits the use of Chicxulub impact spherules as a correlation tool and time horizon without consideration of this temporal and spatial postdepositional history. The following stratigraphic and geographic considerations mitigate this drawback.

1. Only the stratigraphically lowermost (oldest) impact spherule layer in undisturbed sediments provides a marker horizon for the age of the Chicxulub impact. This spherule layer generally contains a calcite matrix and lacks shallow-water debris. In NE Mexico and along the Brazos River in Texas, the stratigraphically lowermost spherule layer is near the base of planktic foraminiferal zone CF1 and predates the K-T boundary by ~300 k.y. This is in agreement with the age of the impact breccia in the Chicxulub crater core Yaxcopoil-1.
2. All stratigraphically higher (younger) spherule layers reflect postdepositional erosion, transport, and redeposition at times of low sea levels, gravity slumps along slopes, or tectonic activity. This is evident in the presence of clastic grains, shallow-water debris, and foraminifera.
3. The first widespread phase of spherule redeposition occurred during the early transgression after the uppermost Maastrichtian sea-level fall (~100–150 k.y. prior to the K-T boundary). At this time, spherules eroded in shallow areas were transported (via gravity flows, slumps) into deep waters via submarine canyons (e.g., NE Mexico and Texas). This phase led to deposition of the spherule layers at the base of the sandstone complex in NE Mexico and Texas, which gave rise to the controversial hypothesis of impact-generated tsunami deposits. The second phase of spherule redeposition occurred during the early Danian zone P1a(1) sea-level low and is mainly found in central Mexico, Guatemala, Belize, and Haiti. A major hiatus marks the K-T boundary in these areas.

4. The stratigraphic proximity of Chicxulub impact spherules and Ir anomaly at or near the K-T boundary in deep-sea sites (e.g., ODP Sites 1049, 1259, and Bass River, New Jersey) does not signify a K-T boundary age for the Chicxulub impact, but may reflect the condensed and often disturbed sedimentary records of the deep sea, which must be carefully evaluated and correlated with the more complete records from NE Mexico and Texas.

CONCLUSIONS

Impact stratigraphy makes use of unique catastrophes in Earth's history and uses their signals in correlation and timing of these events. Impact markers are extremely useful and invaluable tools in stratigraphy with great potential in deciphering a sequence of closely spaced events, such as the timing of the Chicxulub impact and K-T event. But as any sedimentary markers, they are subject to erosion, transport, and redeposition, which can lead to erroneous interpretations. Therefore, the timing of impacts must be deciphered from undisturbed, complete, and continuous sequences with high sedimentation rates. Moreover, the regional stratigraphic distribution is critical to sort out spherule layers that are redeposited from those that represent the original impact ejecta fallout. This study shows that in undisturbed sequences of NE Mexico and Brazos River, Texas, the Chicxulub spherule ejecta and K-T Ir anomaly and red layer are widely separated, with biostratigraphy indicating ~300,000 yr elapsed between these two events. In all other regions examined, the stratigraphic records are demonstrably incomplete, with Chicxulub spherule ejecta redeposited in early Danian sediments (e.g., Cuba, Haiti, Belize, Guatemala, central Mexico), or juxtaposed at unconformities at the K-T boundary (Bass River, New Jersey, Blake Nose, NW Atlantic). For the K-T transition, impact stratigraphy predates the K-T boundary and Ir anomaly. There is also evidence that the environmental upheaval continued during the early Danian with another smaller impact and volcanism.

The story that has emerged to date is that the K-T transition was a time of long-term upheavals including multiple impacts, volcanism, and rapid climate changes that eventually led to the mass extinction, but comprehensive studies are still lacking. Deciphering the full history of the K-T mass extinction will require further detailed regional and global studies. For example, a comprehensive study is needed to evaluate the geochemical similarities and differences between the Chicxulub impact spherules and the rare clay spherules observed in some K-T clay layers, which may reveal their source. Global studies are needed to evaluate the geographic distribution of the Chicxulub impact spherule layer, which currently is restricted largely to Central America and the Caribbean. The absence of this spherule layer in geographically more distant regions suggests that the search has concentrated on the K-T boundary interval, instead of the latest Maastrichtian, or that this impact was too small to have a global distribution and global environmental effects. Perhaps for too long has the search for the cause of the K-T mass extinction concentrated almost exclusively on a large impact while ignoring Deccan volcanism, the other major catastrophe on Earth 65 m.y. ago. Recent studies suggest that the ultimate cause may well have been the combined effects of volcanism and impacts.

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